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# MINERALOGICAL JOURNAL

CONTENTS

Announcement ..... 1
On the Dielectric Constants of Minerals ..... J. Takubo, Y. Ukai and S. Kakitani... 3
On the Dielectric Constants of Rocks ..... J. Takubo, Y. Ukai and Cheng Chi Kuo...25
The Differential Thermal Analysis Curves and the Dehydration Curves of Zeolites ..... M. Koizumi...36
On Conichalcite from Kitabira, Yamaguchi Prefecture, Japan ..... H. Minato and Y. Takano...48
Suanite, a New Magnesium Borate Mineral from Hol Kol, Suan, North Korea ..... T. Watanabe...54

*Short Communications*

Recueil Minéralogique I. (1) Épidote de Munam. (2) Épidote de Takéshi ..... J. Ito...63
Particle Shape of a Certain Clay of Hydrated Halloysite, as Revealed by the Electron Microscope ..... T. Sudo...66

**The Mineralogical Society of Japan**
Department of Geology and Mineralogy, Faculty of Science,
Hokkaido University, Sapporo, Japan

# MINERALOGICAL JOURNAL

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# ANNOUNCEMENT

After a prolonged and thorough discussion on the necessity in this country of a society exclusively devoted to the promotion of mineralogical sciences, we have ventured to create the Mineralogical Society of Japan. An inaugural meeting of the chartered members of the Society was held at the University of Tokyo, June 30, 1952. The following officers were elected in accordance with Rules previously adopted:

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The object of the Society is to promote the study of mineralogy and related sciences, and further to bring those who are engaged in mineralogical research in this country into more concerted activities than hithertofore for their benefit. The Society earnestly desires to co-operate with the colleagues the world over for the advancement of mineralogy.

It is being planned to issue two series of publications as the organs of the Society: "KOBUTSUGAKU ZASSHI" (Journal of the Mineralogical Society of Japan) and "MINERALOGICAL JOURNAL". No. 1, No. 2 and No. 3 of the former series have already been published in September, 1952, January, 1953 and May, 1953 respectively. We are herewith presenting the latter series.

The Editors should like to take this opportunity to ask those concerned to help us make the activity of our Society effective. Critical suggestions from the reader as to the conducts of the Editors will be gratefully appreciated, and any paper of mineralogical interest submitted for the possible publication in the Journal will be carefully considered.

THE EDITORS

MINERALOGICAL JOURNAL, VOL. 1, No. 1, PP. 3-24, SEPTEMBER, 1953

# ON THE DIELECTRIC CONSTANTS OF MINERALS

## (The Determinations of Dielectric Constants of Minerals and Rocks[25] and their Applications to the Mineralogical and Geological[23] Studies, Part 1)

JITSUTARO TAKUBO, YASUO UKAI and SATORU KAKITANI

*Geological and Mineralogical Institute, Faculty of Science, University of Kyoto.*

1127R

### *Preface*

The dielectric constants of minerals have been determined by numerous investigators to whom L. Boltzman,[2] L. Graetz,[8] L. Fomm, W. M. Thornton,[27] J. Curie,[3] Th. Liebish,[13] H. Rubens, W. Schmidt,[19] J. Takubo[22] are included. W. Schmidt has determined the dielectric constants of various minerals using the immersion method and their values have been hitherto under the most utilization. According to the Maxwell's[7] theory, the dielectric constants of non-metallic crystals such as sulfur and diamond which are constructed from a single element are related to the refractive indices by the simple formula as $n^2=\varepsilon$. But common ionic crystal exhibits some of the three kinds of polarizations[6] under the electromagnetic vibration with appropriate frequencies. The maximum dielectric loss owing to the electronic polarization arises on the frequency of visible or infra-violet ray, and that owing to the atomic polarization arises on the infra-red frequency.

In addition to these polarizations, the dipolar substances have orientational polarization due to the orientational displacement of dipole. In the case of common ionic crystals,[24] therefore they should show higher dielectric constants than those obtained by squaring the refractive indices owing to other polarizations beside the electronic one and do not satisfy the Maxwell's formula. Notwithstand-

ing of this fact, the dielectric constants generally show analogous changes to those of refractive indices. Therefore, the mineralogical studies which have been carried on by the determinations of the refractive indices should be made more effectively by the determinations of the dielectric constants. From the above reasons, the writers dare say that the study of dielectric constant shall be developed to the important researching method of mineralogy in near future.

### *Measuring methods of dielectric constants*

For the measurements of dielectric constants, two following methods were adopted.

*Measurement by ultra short wave-length.*[2)] The Barkhausen and Kurz[1)] vibration of ultra short wave length such as 101.43 cm. was excited by using a vacuum tube US 6B made by the Japan Wireless

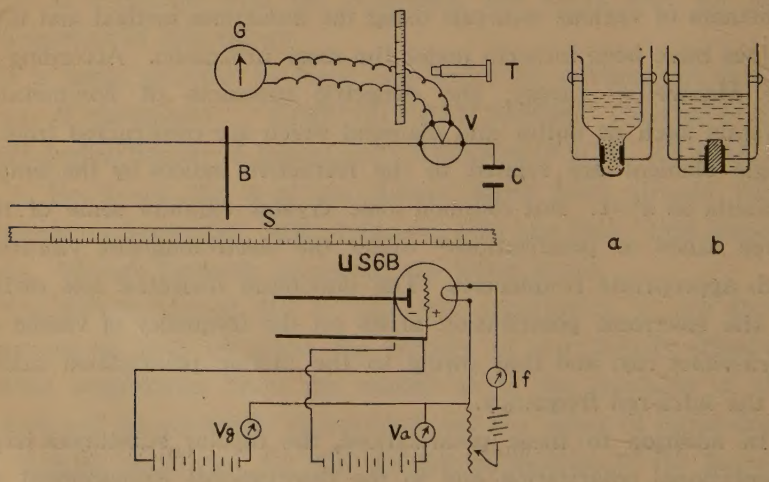


Fig. 1. Apparatus of Lecher's system by ultra short wave.

*G*: Galvanometer *S*: Scale *B*: Metal Bridge *T*: Telescope
*V*: Vacuum Thermo-couple *C*: Condencer (a, b)
$V_g$: Volt-meter of Grit $V_a$: Volt-meter of Anode
$I_f$: Ampere-meter of Filament.

Telephony Company and it was resonated with the Lecher's system connected to a condenser. The exact syntonization may be ascertained from the deflection of galvanometer which was connected to a vacuum thermo-couple inserted to Lecher's system. The whole apparatus is indicated in Fig. 1.

The condencer was connected with the parallel lying Lecher wires. Thus a circuit was made, consisting of the Lecher wires, metal bridge and the condenser. The circuit was resonated with the radiated electromagnetic wave by means of sliding the metal bridge and the position of it was read on the scale at just time when the maximum syntonization was ascertained by the deflection of galvanometer. As the standard solution, we used the acetone, benzene and several mixed solutions of them. The scale reading was obtained with the condencer containing suitable amount of a standard solution. After the same procedure was repeated respectively with each standard solution, the curve representing the relation between the scale readings and the dielectric constants of the standard solutions was made. In this way, the operations were undertaken with the condenser containing both the standard solution and the mineral specimen and another curve was made from the thus obtained scale readings. The dielectric constant of the mineral under consideration was determined, corresponding to that of a cross point of these two curves.

The condenser (b) was used for the polished plate and (a), for the powder sample of the mineral.

*Measurement by moderate wave length such as 500 kc.*[17] The measuring apparatus is shown in Fig. 2.

The standard frequency wave excited by the emissioner (O) is syntonized by means of (L) and ($L_c$). The immersion method was applied as in the case of (A). The condenser ($C_x$) containing standard solution and mineral may be syntonized by changing the capacity of standard condenser ($C_s$). The dielectric constant of mineral corresponds with that of the intersection of two curves, of

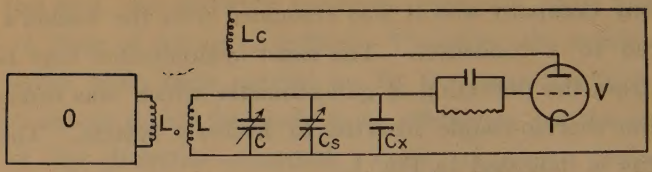


Fig. 2. Measuring apparatus for 500 kc. frequency.

O: Standard ossilator
$L_o$: Ossilation coil
L: Resonance coil
$L_c$: Regeneration coil
C: Resonance condenser
$C_s$: Standard condenser
$C_x$: Condenser with Sample
V: Autodyne coherer.

which one curve relates to the dielectric constants of standard solutions and readings of capacities of standard condenser ($C_s$), and other relates to those obtained by using condenser ($C_x$) containing a mineral immersed in the standard solution. The cell constant of ($C_x$) condenser was determined with distilated pure acetone made by Merk Company accepting its dielectric constant as 19.54 at 18°C. The dielectric constants of mixed standard solutions of acetone and benzene in various proportions were measured by using the determined cell constant. These results are shown in the following Table.

Table 1

| Acetone % | ε | | Acetone % | ε | |
|---|---|---|---|---|---|
| | 1 | 2 | | 1 | 2 |
| 0 | 2.28 | 2.25 | 35.0 | 7.14 | 7.62 |
| 9.8 | 3.52 | 3.49 | 40.0 | 8.01 | 8.23 |
| 15.0 | 4.31 | 4.23 | 45.0 | 8.79 | 9.09 |
| 20.0 | 5.05 | 4.98 | 49.5 | 9.81 | 9.90 |
| 25.0 | 5.88 | 5.78 | 60.0 | 11.48 | 11.87 |
| 31.0 | 6.64 | 6.73 | 69.4 | —— | 13.85 |

ε 1: D. C. determined with 500 kc. in frequency
ε 2: D. C. determined with 76 cm. in wave length by W. Schmidt[20].

## *Experimental results*

*The dielectric constants of various kinds of minerals.* With the above mentioned methods, the dielectric constants of various kinds of minerals were determined. The results are summarized as follows.

Table 2

| Mineral | locality | ε (1) | ε (2) | ε (3) |
|---|---|---|---|---|
| Garnet | Wada-toge, Nagano Pref. | 11.58 | 12.71 | |
| Zincblende | Ani-mine, Akita Pref. | 7.90 | 7.60 | |
| | Chichibu-mine, Saitama Pref. | 7.90 | | |
| | Nakatatsu-mine, Fukui Pref. | 12.13 | | |
| | Zoplin, Misori, U. S. A. | 7.90 | | |
| | Claustal, Harz. | 7.88 | | |
| Fluorite | Akenobe-mine, Hyogo Pref. | 6.26 | | |
| | Aokawa, Wakayama Pref. | | 6.28<br>6.21 | 6.69 |
| | Ikuno-mine, Hyogo Pref. | 6.28 | | |
| | Gonberg, Schweiz. | 6.26 | | |
| | Durham, England. | 6.33<br>6.26 | | |
| | Freiberg, Sachsen | 6.63<br>6.58 | | |
| Opal | Bodai, Ishikawa Pref. | 7.18 | 18 10 | |
| | Hōsaka, Fukushima Pref. | 7.43 | 22 30 | |
| Agate | unknown | 7.43 | 44 40 | |
| Rock Salt | Huetra von Sal | 5.55<br>5.55<br>5.56 | | |
| | Stassfurt, Sachsen | 5.40 | | |
| Hyalite | Tateyama, Toyama Pref. | 4.12<br>4.22 | 4 51 | |
| Chalcedony | Tateyama, Toyama Pref. | 5.48 | | |
| Analcime | Seiser Alp. Tirol | 5.88<br>5.87 | | |
| Leucite | Albanergebirge, Italy | 7.08<br>7.13<br>7.18 | | |
| Calcite | Kamioka-mine, Toyama Pref. | ⊥c 8.60 | ⊥c 8.15 | 8.35 |
| | | //c 7.88 | //c 7.41 | |
| | Taio-mine, Fukuoka Pref. | ⊥c 8.49 | | |

Table 2 —*Continued*

| | | | | | |
|---|---|---|---|---|---|
| | | //c | 7.87 | | |
| | | ⊥c | 8.53 | | |
| | | //c | 7.87 | | |
| | Cumberland | ⊥c | 8.50 | | |
| | | //c | 7.82 | | |
| Tourmaline | Ishikawa-yama, Fukushima Pref. | ⊥c | 6.83 | | |
| | | //c | 5.43 | | |
| | Ashiya-mine, Yamanashi Pref. | ⊥c | 6.82 | ⊥c 6.82 | |
| | | | | //c 5.60 | |
| | Ceylon | ⊥c | 6.68 | | |
| | | //c | 5.43 | | |
| | | ⊥c | 6.82 | | |
| | | //c | 5.61 | | |
| Dolomite | Binnental, Schweiz. | | | | |
| | | ⊥c | 7.50 | | |
| | | //c | 6.15 | | |
| | | ⊥c | 7.56 | | |
| | | //c | 6.07 | | |
| Beryl | Mursinka, Uralgebirge | ⊥c | 6.18 | | |
| | | //c | 5.67 | | |
| | | ⊥c | 6.17 | | |
| | | //c | 5.67 | | |
| | | ⊥c | 6.18 | | |
| | | //c | 5.67 | | |
| | Madagascar | | | ⊥c 6.59 | 6.68 |
| | | | | //c — | |
| Apatite | Ashio-mine, Tochigi Pref. | ⊥c | 9.47 | ⊥c 11.14 | |
| | | //c | 7.62 | //c 10.27 | |
| | | ⊥c | 10.20 | | |
| | | //c | 7.62 | | |
| | Kamioka-mine, Gifu Pref. | ⊥c | 9.48 | | |
| | | //c | 7.43 | | |
| Quartz | Naegi-cho, Gifu Pref. | ⊥c | 4.10 | | |
| | | //c | 4.22 | | |
| | Mt. Hira, Shiga Pref. | | | ⊥c — | |
| | | | | //c 4.52 | |

Table 2 — *Continued*

| | | | | | | |
|---|---|---|---|---|---|---|
| | Mt. Kinpo, Yamanashi Pref. | ⊥c | 4.13 | | | |
| | | //c | 4.28 | | | |
| | Cumberland | ⊥c | 4.09 | | | |
| | | //c | 4.48 | | | |
| | | ⊥c | 4.08 | | | |
| | | //c | 4.32 | | | |
| Diaspore | Mitsuishi-mine, Okayama Pref. | ⊥a | 7.70 | | | |
| | | ⊥b | 8.38 | | | |
| | | ⊥c | 7.27 | | | |
| | | ⊥a | 7.71 | | | |
| | | ⊥b | 8.37 | | | |
| | | ⊥c | 7.30 | | | |
| Sulphur | Perticara, Rimini, Italy | ⊥a | 3.44 | | | |
| | | ⊥b | 3.66 | | | |
| | | ⊥c | 4.30 | | | |
| | | ⊥a | 3.43 | | | |
| | | ⊥b | 3.61 | | | |
| | | ⊥c | 4.24 | | | |
| Topaz | Naegi-cho, Gifu Pref. | ⊥a | 6.31 | ⊥a | 6.66 | |
| | | ⊥b | 6.44 | ⊥b | 6.58 | 6.61 |
| | | ⊥c | 6.28 | ⊥c | 6.48 | |
| | | ⊥a | 6.34 | | | |
| | | ⊥b | 6.42 | | | |
| | | ⊥c | 6.29 | | | |
| Aragonite | Bilin, Böhmen | ⊥a | 9.58 | | | |
| | | ⊥b | 7.28 | | | |
| | | ⊥c | 6.26 | | | |
| | Matsushiro-mine, Shimane Pref. | | | ⊥a | 9.31 | |
| | | | | ⊥b | 7.19 | |
| | | | | ⊥c | 6.59 | |
| Baryte | Kamioka-mine, Gifu Pref. | ⊥a | 7.70 | | | |
| | Shodo-mine, Korea | ⊥a | 7.80 | | | |
| | Trintington, England | ⊥a | 7.80 | ⊥a | 7.85 | |
| | | ⊥b | 12.33 | ⊥b | 12.00 | |
| | | ⊥c | 7.85 | ⊥c | 7.82 | |

Table 2—*Continued*

| | | | | |
|---|---|---|---|---|
| Celestin | Girgemt, Sizilien | ⊥a 7.58 | | |
| | | ⊥b — | | |
| | | ⊥c 8 25 | | |
| | | ⊥a 7.61 | | |
| | | ⊥b — | | |
| | | ⊥c 8.27 | | |
| Damburite | Toroku, Miyazaki Pref. | | ⊥a 6.35 | |
| | | | ⊥b 6.34 | |
| | | | ⊥c 6.58 | 6.67 |
| | | | ⊥a — | |
| | | | ⊥b 6.34 | |
| | | | ⊥c 6.77 | |
| Gypsum | Hanaoka-mine, Akita Pref. | ⊥b 4.98 | | |
| | | ⊥b 5.02 | ⊥b 5.00 | |
| Vivianite | Ashio-mine, Tochigi Pref. | ⊥b 6.07 | | |
| | | ⊥b 6.08 | ⊥b 6.34 | |
| Epidote | Zalzbachtal, Tirol | ε Ⅰ 7.69 | | |
| | | ε Ⅱ 10.11 | | |
| | | ε Ⅲ 15.39 | | |
| Moonstone | Binzan, Korea | //(100) 5.71 | | |
| | | //(010) 5.96 | | |
| | | //(001) 5.71 | | |
| | | //(100) 5.77 | | |
| | | //(010) 6.01 | | |
| | | //(001) 5.76 | | |
| Allanite | Sandaiko, Manchuria | | 19.40 | 10.40 |
| | | | 19.40 | 10.90 (800°C) |
| | Mt. Suisho, Fukushima Pref. | | 29.10 | |
| | | | 25.90 | 14.10 |
| | | | 16.10 | 14.10 (800°C) |
| | Morimoto, Kyoto Pref. | | 12.50 | 12.50 |
| | | | | 14.30 (800°C) |
| | Angaku, Korea | | 14.80 | 17.10 |
| | | | | 11 20 (800°C) |
| | Tatsurido, Korea | | 15.63 | 14.00 |

Table 2 —*Continued*

| | | | | |
|---|---|---|---|---|
| | | | | 14.90 (800°C) |
| Tscheffkinite | Kawabe, Kyoto Pref. | | 25.30 | |
| Yttrianite | Iisaka, Fukushima Pref. | | | 11.30 |
| | | | | 11.20 (800°C) |
| Gadolinite | Arendal, Norway | | 11.00 | 11.50 |
| | | | | 10.20 (800°C) |
| | Hittero, Norway | | | 10.30 |
| | | | | 9.70 (800°C) |
| Ampangabeite | Madagascar | | 22.80 | 22.50 |
| | | | | 24.20 (800°C) |
| Orangite | Norway | | | 13.20 |
| | | | | 13.00 (800°C) |
| Blomstrandite | Hittero, Norway | | | 16.60 |
| | | | | 22.90 (800°C) |
| Lessingite | Heiko, Korea | | 17.60 | |
| Monazite | Tetsuzan, Korea | | 11.90 | |
| Yttrotitanite | Arendal, Norway | | | 19.00 |
| | | | | 20.90 (800°C) |
| Ellsworthite | Ontario, Canada | | | 17.60 |
| | | | | 40.00 (800°C) |
| Kobeite | Kawabe, Kyoto Pref. | | | 19.50 |
| | | | | 27.20 (800°C) |
| Tantalite | Marblo Bar | | | 26.40 |
| | Greenbushes | | | 26.70 |
| | Brazil | | | 28.10 |
| Columbite | Ginkoku, Korea | | | 36.70 |
| | | | | 43.30 (800°C) |
| | Tanyo, Korea | | | 23.70 |
| | | | | 22.80 (800°C) |
| | Ishikawayama, Fukushima Pref. | | | 45.80 |
| Samarskite | North Calorina, U. S. A. | | 28.90 | 30.60 |
| | | | | 56.00 (800°C) |
| | Mitchel Co., North Calorina | | 36.20 | |
| | | | 31.80 | 33.50 |
| | | | 35.50 | 32.80 (800°C) |
| | Daiboshin, Manchuria | | 25.80 | 24.40 |

Table 2 —*Continued*

| | | | | |
|---|---|---|---|---|
| | | | | 31.40 (800°C) |
| | Arendal, Norway | | | 24.70 |
| | | | | 30.20 (800°C) |
| | Kawabe, Fukushima Pref. | | 25.80 | 28.10 |
| | | | | n. d. (800°C) |
| Fergusonite | Daiboshin, Manchuria | | 21.80 | 19.80 |
| | | | | 19.20 (800°C) |
| | Oro, Kyoto Pref. | | 22.40 | 21.30 |
| | | | | 18.40 (800°C) |
| | Hakata, Ehime Pref. | | 29.10 | 22.10 |
| | | | | 18.60 (800°C) |
| Euxenite | Sandaiko, Manchuria | | 25.20 | 23.60 |
| | | | 24.80 | 29.90 (800°C) |
| | Brevig, Norway | | 23.70 | 22.30 |
| | | | | 26.20 (800°C) |
| | North Calorina, U.S.A. | | | 25.30 |
| | | | | 32.70 (800°C) |

In the above Table, $\varepsilon(1)$ and $\varepsilon(2)$ show the dielectric constants determined respectively with the wave having 101.43 cm. in length and 500 kc. wave using a thin plate of the mineral, and $\varepsilon(3)$ those of the powder specimens pulverized into 80–100 mesh with 500 kc. wave. The dielectric constants of massive specimens having no defined crystal faces or of fine grained specimens which can not be polished into thin plates were measured with pulverized powders. $\perp$a, $\perp$b and $\perp$c stand for the thin plates perpendicular to crystal axes a, b and c, //a, //b and //c the parallel sections to each axis and //(100), //(010) and //(001) the parallel sections to the crystal faces (100), (010), (001). On the metamict minerals, measurements were made either with the original and crystallized specimens which were preheated at 800°C.. These values of the latter are distinguished from those of former by denoting 800°C.. According to the above described results, no remarkable difference can be recognized between the two dielectric constants which were measured with

ultra short wave 101.43 cm. and intermediate frequency wave 500 kc.. But on the dielectric constants measured by 500 kc. wave, the hydrated amorphous or cryptocrystalline minerals such as opal, agate show, however, more significant high dielectric constants than that of non-hydrated quartz. This phenomena[26] should be ascribed to the orientational polarization of dipole substances. The minerals having the complicated chemical composition such as allanite, tantalite, columbite, samarskite, fergusonite, euxenite and etc. show remarkably higher dielectric constants than those of common silicate minerals and the values of same species are different according to their localities. These facts should be ascribed to the discrepancies of minute chemical compositions according to their localities or to the additions of some dipole substances. The dielectric constants of the preheated metamict minerals differ from those of non-heated metamict minerals; some increase their values and others decrease.

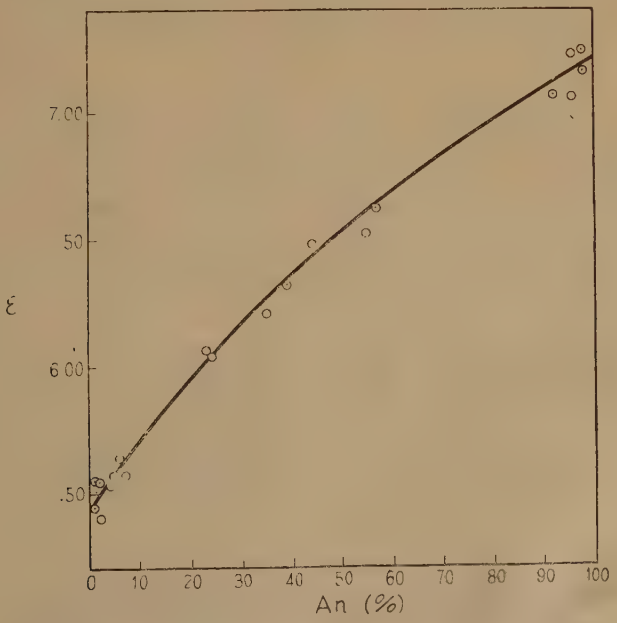


Fig. 3. Relationship between dielectric constant and An-content of plagioclase.

Table 3

| Comp. | (1) Albite[9] | (2) Albite | (3) Albite | (4) Albite | (5) Albite | (6) Albite | (7) Albite | (8) Albite | (9) Oligoclase | (10) Oligoclase[30] |
|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 66.84 | 68.20 | 65.79 | 66.41 | 67.20 | 66.28 | 67.00 | 67.10 | 61.75 | 62.80 |
| $Al_2O_3$ | 19.62 | 19.28 | 21.03 | 20.81 | 19.93 | 20.90 | 20.60 | 20.22 | 23.89 | 23.23 |
| $Fe_2O_3$ | 0.57 | 0.35 | 0.37 | —— | 0.49 | 0.10 | 0.34 | 0.24 | 0.15 | 0.18 |
| CaO | 0.59 | 0.18 | 1.08 | 0.90 | 0.40 | 1.17 | 0.26 | 0.36 | 0.98 | 4.64 |
| MgO | —— | 0.06 | 0.04 | 0.03 | —— | —— | 0.03 | —— | 0.04 | —— |
| $Na_2O$ | 11.53 | 11.55 | 10.93 | 9.88 | 11.32 | 10.48 | 10.83 | 11.39 | 8.70 | 8.51 |
| $K_2O$ | 0.10 | 0.34 | 0.32 | 1.32 | 0.08 | 0.48 | 0.42 | 0.33 | 0 25 | 0.81 |
| $H_2O^+$) | 0.73 | 0.30 | 0.21 | 0.29 | 0.53 | —— | 0.26 | 0.36 | 0.19 | —— |
| $H_2O^-$) | 0.04 | 0.03 | 0.09 | 0.03 | 0.08 | —— | 0.05 | 0.05 | 0.04 | —— |
| Total | 100.02 $Ab_{93}An_7$ | 100.29 $Ab_{99}An_1$ | 99.86 $Ab_{95}An_5$ | 99.67 $Ab_{95}An_4$ | 100.03 $Ab_{98}An_2$ | 99.36 $Ab_{94}An_6$ | 99.79 $Ab_{99}An_1$ | 100.05 $Ab_{98}An_2$ | 99.99 $Ab_{76}An_{24}$ | 100.17 $Ab_{77}An_{23}$ |
| ε | 5.57 | 5.45 | 5.58 | 5.53 | 5.55 | 5.64 | 5.55 | 5.40 | 6.03 | 6.06 |

| Comp. | (11) Andesine | (12) Andesine | (13) Andesine[5)15)] | (14) Labradorite[30)] | (15) Labradorite | (16) Anorthite | (17) Anorthite | (18) Anorthite | (19) Anorthite | (20) Anorthite[32)30)] |
|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 58.60 | 59.03 | 56.39 | 53.87 | 54 94 | 43.79 | 42.70 | 43.20 | 44.18 | 44.77 |
| $Al_2O_3$ | 26.29 | 26.05 | 28.76 | 29.87 | 28.24 | 35.79 | 36.78 | 36.43 | 35.18 | 36.42 |
| $Fe_2O_3$ | 0.24 | —— | 1.00 | 1.33 | 0.12 | 0.43 | 0.31 | 0.43 | 1.03 | 0.08 |
| CaO | 6.80 | 7.51 | 8.96 | 11.05 | 10.92 | 18.68 | 19.44 | 18.91 | 18.30 | 18.98 |
| MgO | 0.02 | —— | —— | —— | 0.12 | 0.33 | 0.52 | tr | 0.10 | 0.10 |
| $Na_2O$ | 7.00 | 6.60 | 6.30 | 4.60 | 4.98 | 0.42 | 0.23 | 0 23 | 0.71 | 0.40 |
| $K_2O$ | 0.18 | 0.75 | 0.75 | 0.02 | 0.68 | 0.03 | 0.03 | 0.03 | 0.03 | 0.02 |
| $H_2O^+$) | 0.41 | —— | —— | 0.21 | —— | 0.59 | 0.61 | 0.61 | 0.85 | —— |
| $H_2O^-$) | 0.06 | —— | —— | 0.12 | —— | 0.06 | 0.08 | 0.08 | 0.08 | —— |
| Total | 99.60 $Ab_{65}An_{35}$ | 99.94 $Ab_{61}An_{39}$ | 101.72 $Ab_{56}An_{44}$ | 101.07 $Ab_{43}An_{57}$ | 100.40 $Ab_{45}An_{55}$ | 100.13 $Ab_4An_{96}$ | 100.28 $Ab_2An_{93}$ | 99.92 $Ab_2An_{93}$ | 100.46 $Ab_7An_{93}$ | 100.78 $Ab_4An_{96}$ |
| ε | 6.20 | 6.31 | 6.47 | 6.62 | 6.51 | 7.05 | 7.23 | 7.15 | 7.05 | 7.22 |

*Dielectric constants of rock forming minerals.* The chemical compositions and dielectric constants of common rock forming minerals such as plagioclase-, pyroxene-, amphibole-group minerals were determined. The dielectric constants of these minerals were measured with pulverized powders.

*Plagioclase-group.* The chemical compositions and dielectric constants are shown in Table 3 and An %-ε diagram is shown in Fig. 3.

The relationship between the dielectric constants and An-contents

Table 4—1

| Comp. | (1) | (2) | (3) | (4) | (5) | (6) | (7) |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 57.25 | 47.89 | 52.82 | 44.77 | 50.58 | 39.39 | 49.59 |
| $Al_2O_3$ | 2.65 | —— | 18.02 | 7.67 | 4.24 | 11.29 | 1.14 |
| $Fe_2O_3$ | 3.73 | 10.01 | 3.08 | 4.07 | 4.36 | 12.99 | —— |
| FeO | 4.21 | 2.89 | 4.74 | 4.18 | —— | 4.12 | 23.76 |
| CaO | 2.02 | 0.82 | 3.69 | 24.35 | 22.69 | 29.46 | 22.13 |
| MgO | 29.25 | 35.08 | 17.70 | 14.81 | 17.23 | 3.76 | 1.64 |
| $K_2O$ | $TiO_2$ 0.10 | —— | —— | —— | —— | —— | MnO 1.48 |
| $Na_2O$ | —— | —— | —— | —— | 0.44 | —— | 0.45 |
| $H_2O^-$ | —— | —— | —— | —— | —— | —— | —— |
| $H_2O^+$ | 0.35 | 4.01 | 0.34 | 0.15 | —— | 0.41 | —— |
| Total | 99.56 | 100.70 | 100.39 | 100.00 | 99.54 | 101.42 | 100.19 |

| Comp. | (8) | (9) | (10) | (11) | (12) | (13) |
|---|---|---|---|---|---|---|
| $SiO_2$ | 50.07 | 53.56 | 50.18 | 51.00 | 63.25 | 51.77 |
| $Al_2O_3$ | —— | 0.26 | 2.80 | 12.41 | 27.65 | 6.71 |
| $Fe_2O_3$ | —— | 2.75 | —— | 2.27 | 0.53 | —— |
| FeO | 24.04 | 8.69 | 12.50 | 8.05 | 0.42 | 1.27 |
| CaO | 21.41 | 30.16 | 17.79 | 14.49 | 0.83 | 37.92 |
| MgO | 3.25 | 1.70 | 13.54 | 6.32 | —— | —— |
| $K_2O$ | —— | —— | —— | 0.23 | —— | —— |
| $Na_2O$ | —— | 2.64 | —— | 5.12 | 1.35 | —— |
| $H_2O^-$ | —— | —— | —— | —— | 5.81 | —— |
| $H_2O^+$ | 0.33 | —— | 1.02 | —— | 0.23 | 1.03 |
| Total | 99.10 | 99.76 | 97.83 | 99.89 | 100.07 | 98.70 |

Table 4—2

| Nominated Mineral | $R^{II}SiO_3$ | | | Main-composition | ε | Extinction Angle | Locality |
|---|---|---|---|---|---|---|---|
| | $MgSiO_3$ | $CaSiO_3$ | $FeSiO_3$ | | | | |
| (1) Enstatite | 90.0 | 4.5 | 5.5 | (Mg, Fe, Ca) $SiO_3$ | 5.66 | 0°00′ | Norwegen |
| (2) Enstatite | 94.1 | 1.6 | 4.3 | (Mg, Fe Ca) $SiO_3$ | 6.15 | 10°30′ | Arifuku |
| (3) Bronzite | 76.9 | 11.5 | 11.6 | (Mg, Fe, Ca) $SiO_3$ | 7.50 | 13°10′ | Steinmark |
| (4) Diopside | 42.7 | 50.4 | 6.9 | (Ca, Mg, Fe) $SiO_3$ | 7.64 | 38°40′ | Schweiz |
| (5) Diopside | 51.2 | 48.8 | 0.0 | (Mg, Ca) $SiO_3$ | 7.90 | 41°50′ | Kamisano[10] |
| (6) Hedenbergite | 8.5 | 77.7 | 13.8 | (Ca, Fe, Mg) $SiO_3$ | 9.22 | 56°40′ | Nordomarken |
| (7) Hedenbergite | 5.3 | 50.0 | 44.7 | (Ca, Fe, Mg) $SiO_3$ ……85<br>$NaAl(SiO_3)_2$ ……1 | 9.17 | 55°30′ | Obira |
| (8) Hedenbergite | 9.6 | 45.8 | 44.6 | (Ca, Fe, Mg) $SiO_3$ | 9 25 | 55°00′ | Kamioka |
| (9) Augite | 6.0 | 76.9 | 17.1 | (Ca, Fe, Mg) $SiO_3$ ……1<br>$NaAl(SiO_3)_2$ ……16 | 9.16 | 66°00′ | Yoneyama[11] |
| (10) Augite | 38.9 | 40.9 | 20.2 | (Ca, Mg, Fe) $SiO_3$ ……30<br>(Mg, Fe) $(Al, Fe)_2 SiO_6$ …1 | 8.89 | 66°50′ | Nishigatake [18][12] |
| (11) Aegirine | 29.7 | 49.0 | 21.3 | (Ca, Mg, Fe) $SiO_3$ ……9<br>$NaAl(SiO_3)_2$ ……2<br>(Mg, Fe) $(Al, Fe)_2 SiO_3$ …1 | 9.05 | 67°00′ | Norwegen |
| (12) Spodumen | | | | $LiAl(SiO_3)_2$ | 8.45 | 30°30′ | Stering |
| (13) Wollastonite | | | | $CaSiO_3$ | 7.80 | 0°00′ | |

of plagioclases can be shown by the following formula, $\varepsilon = 5.473 (\pm 0.016) + 0.00241 (\pm 0.00010)\,An - 0.000070 (\pm 0.000010)\,An^2$. Where An denotes the contents of anorthite by percentage. From this experimental formula, the An contents may be easily calculated by measuring the dielectric constant without chemical analysis or microscopic determination.

*Pyroxene-group*[14),31),4),21),15)]. The chemical compositions and dielectric constants of pyroxene-group minerals are indicated in Table 4-1 and Table 4-2.

The molecular percentage of $MgSiO_3$ and $\varepsilon$ are related in Fig. 4.

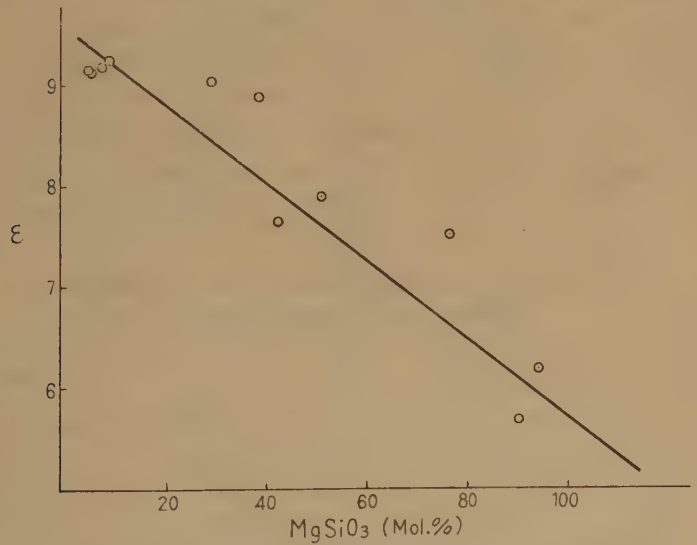


Fig. 4. $\varepsilon$-$MgSiO_3$ content diagram of pyroxene.

The increase of molecular percentage of $MgSiO_3$ proportionally decreases the dielectric constants of minerals. The dielectric constants of pyroxenes which contain $MgSiO_3$ less than 17% are above 9, $MgSiO_3$ 17–44% show 9–8, $MgSiO_3$ 44–72% 8–7, $MgSiO_3$ 72–100% lower than 7. The $CaSiO_3$ and $FeSiO_3$ components present almost no different influence upon the dielectric constant of pyroxene. Accepting the facts that the dielectric constant of pyroxene is

remarkably effected by the $MgSiO_3$ component and have no different influence by $CaSiO_3$ or $FeSiO_3$, the three components and ε of pyroxene-group minerals are related as the following diagram.

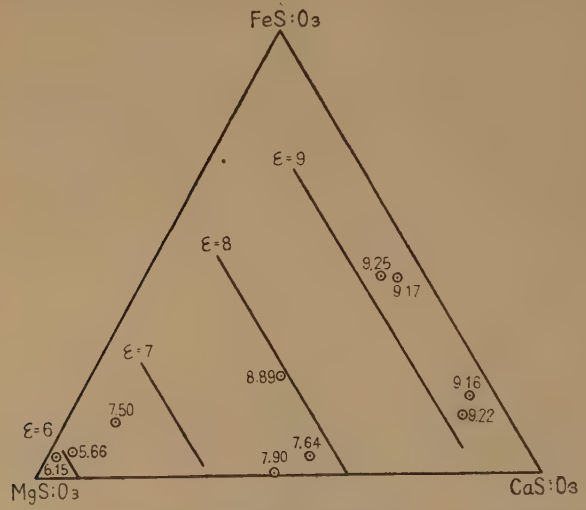


Fig. 5. Diagram showing the relation of three components ($MgSiO_3$, $CaSiO_3$, $FeSiO_3$) and ε.

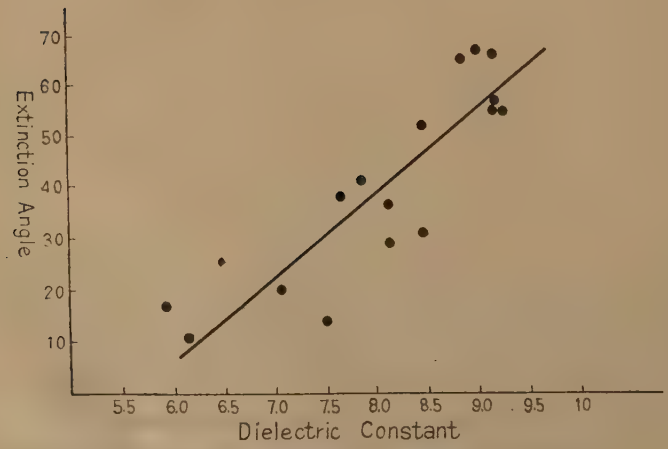


Fig. 6. Relationship between dielectric constant and extinction angle of pyroxene.

Wollastonite differs in the crystal structure from other pyroxene minerals and shows lower dielectric constant notwithstanding its negligible small amount of $MgSiO_3$ component. On the alkali-bearing pyroxene, the dielectric constant of jadate is lower than that of spodumen and that of aegirine is relatively high. As is shown in Fig. 6 showing the relation between the extinction angles and dielectric constants, the increase of extinction angle shows a tendency to increase the dielectric constants.

*Amphibole-group*[28),29)]. The amphibole-group minerals generally contain more $R_2^{III}O_3$, $R_2^{I}O$ and $H_2O$ components comparing with the pyroxene-group minerals. Accordingly, these components should be accounted for the dielectric constants of amphiboles. From the analytical results, the molecular ratio $R_2^{I}O : R^{II}O : R_2^{III}O_3 : H_2O$ and $MgSiO_3 : CaSiO_3 : FeSiO_3$ were calculated and these values as well as the dielectric constants and extinction angles of these minerals are shown in Table 5.

Table 5

| Nominated-Mineral | $R_2^{I}O$ | $R^{II}O$ | $R_2^{III}O_3$ | $H_2O$ | $R^{II}SiO_3$ | | | ε | Ext. Angle |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Mg $SiO_3$ | Ca $SiO_3$ | Fe $SiO_3$ | | |
| 1 Actinolite | | 82.42 | 4.45 | 13.13 | 63.68 | 27.19 | 9.13 | 6.23 | 15°30′ |
| 2 Actinolite | | 89.85 | 2.58 | 7.57 | 60.31 | 25.26 | 14.43 | 6.60 | 17°30′ |
| 3 Tremolite | | 68.61 | 20.23 | 11.16 | 6.85 | 85.38 | 7.77 | 8.65 | 27°40′ |
| 4 Tremolite | | 82.19 | 17.30 | 0.51 | 29.46 | 69.20 | 1.34 | 6.80 | —— |
| 5 Tremolite | | 84.05 | 11.76 | 4.19 | 75.64 | 24.36 | | 5.95 | 16°50′ |
| 6 Hornblende | | 63.24 | 19.16 | 17.60 | 32.64 | 32.40 | 34.96 | 8.90 | 40°30′ |
| 7 Hornblende | 3.93 | 83.15 | 4.58 | 8.34 | 59.64 | 24.71 | 15.65 | 7.15 | 19°50′ |
| 8 Hornblende | | 62.83 | 22.80 | 14.37 | 39.39 | 41.89 | 18.72 | 7.11 | 24°10′ |
| 9 Hornblende | | 70.08 | 14.01 | 15.91 | 33.97 | 33.32 | 32.71 | 7.90 | 25°20′ |
| 10 Hornblende | 5.36 | 66.53 | 25.68 | 2.43 | 58.44 | 38 27 | 3.29 | 8.45 | 25°20′ |
| 11 Hornblende | | 64.01 | 20.10 | 15.89 | 50.07 | 37.27 | 12.66 | 10.40 | 37°40′ |
| 12 Hornblende | | 70.49 | 20.08 | 9.43 | 52.56 | 35.83 | 11.61 | 8.55 | 28°50′ |
| 13 Hornblende | | 65.25 | 17.01 | 17.74 | 5.53 | 30.69 | 63.78 | 7.85 | —— |
| 14 Riebeckite | 24.34 | 53.26 | 19.74 | 2.66 | 16.94 | 0.00 | 83.06 | 7.23 | 63°00′ |

The dielectric constants of amphibole minerals change their values according to the ratio of MgO, (Ca, Fe) O, $(Fe, Al)_2 O_3$, $Na_2O$ and $H_2O$ contents. Of these components, $H_2O$ is almost always contained and $Na_2O$ is negligible excepting some special minerals, so that the ratio MgO : (Ca, Fe) O : $(Al, Fe)_2 O_3$ of each minerals were calculated in the next Table.

Table 6

| Nominated Mineral | $(Al, Fe)_2 O_3$ | (Fe, Ca) O | MgO | Locality |
|---|---|---|---|---|
| 1 Actinolite | 5.19 | 39.85 | 48.36 | Daishōji |
| 2 Actinolite | 7.55 | 21.81 | 45.89 | Mähren |
| 3 Tremolite | 23.33 | 58.78 | 3.09 | Nagahara |
| 4 Tremolite | 34.25 | 29.34 | 36.41 | Tessin |
| 5 Tremolite | 12.48 | 27.07 | 60.45 | Anto, China |
| 6 Hornblende | 41.25 | 44.93 | 13.81 | Mushiana |
| 7 Hornblende | 10.25 | 45.84 | 43.91 | Norwegen |
| 8 Hornblende | 44.79 | 38.09 | 17.12 | Fukuoka[33] |
| 9 Hornblende | 36.39 | 48.00 | 15.59 | Schweisberg |
| 10 Hornblende | 49.98 | 25.14 | 24.88 | Böhmen |
| 11 Hornblende | 44.39 | 33.24 | 22.37 | Taihoku |
| 12 Hornblende | 45.37 | 30.90 | 23.73 | Nitatōge |
| 13 Hornblende | 36.99 | 60.86 | 2.15 | Norwegen |
| 14 Riebeckite | 53.76 | 40.65 | 5.59 | Portuga |

The dielectric constants of amphibole minerals are so effected by their high contents of $R_2^{III}O_3$ as is shown in Table 5, that there is no regular relationship between the $R^{II}O$ components and $\varepsilon$ excluding the $R_2^{III}O_3$ components. From Table 6 these three components are related to the dielectric constants as diagrammatically shown in Fig. 7.

It is noticeable that three kinds of mineral groups are distinguished among the amphibole minerals; two groups are plotted on the broken lines and the other is not belonged to these group. The minerals of the first group which contain relatively small amounts of $R_2O_3$ and over than 80% of $R^{II}O$ consisted with 24–27% CaO are

shown by a general formula $H_2O \cdot 2CaO \cdot 5(Mg, Fe)O \cdot 8SiO_2$ corresponding to the tremolite-actinolite series in amphibole-group. The dielectric constants of these minerals increase proportionately with the decrease of MgO or increase of FeO. On the contrary, the minerals of the second group contain 30-40% of CaO and larger amount of $R_2^{III}O_3$ component than those of the first group, so that the effects of $R_2^{III}O_3$ component upon dielectric constant must be considered. As in the Fig. 7, the minerals of the second group also show a regular relationship between the dielectric constants and three components by considering the $R_2^{III}O_3$ component. Generally, the $R_2^{III}O_3$ components enlarge the dielectric constant more than the (Ca, Fe) O components in $R^{II}O$ do. Other minerals which do not belong to these two groups are alkali-bearing amphible or significantly weathered minerals which show no characteristic properties of amphibole. The alkali-bearing amphiboles have relatively low dielectric constants. Therefore the direct relation between

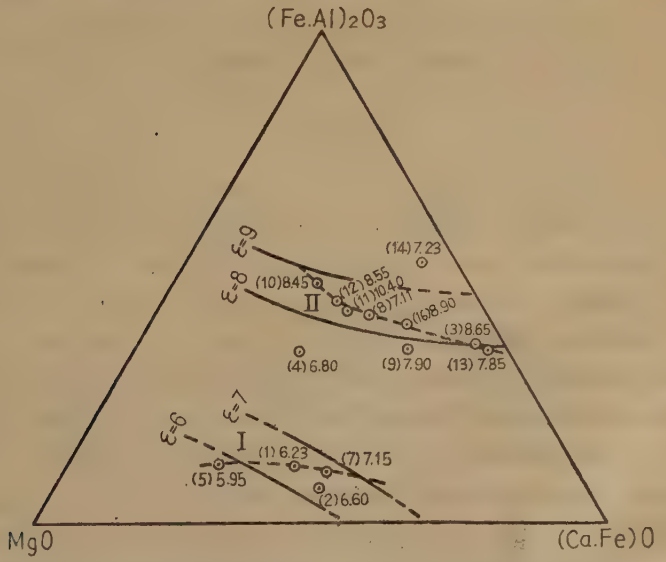


Fig. 7. Diagram showing the relation of three components MgO, (Ca, Fe) O, $(Fe, Al)_2O_3$ and $\varepsilon$.

MgO-contents and dielectric constants was not recognized on the amphibole minerals. On the other hand, the amphibole minerals have more regular relations than pyroxene minerals considering the extinction angles and dielectric constants as shown in Fig. 8. The higher the dielectric constant is, the larger the extinction angle is.

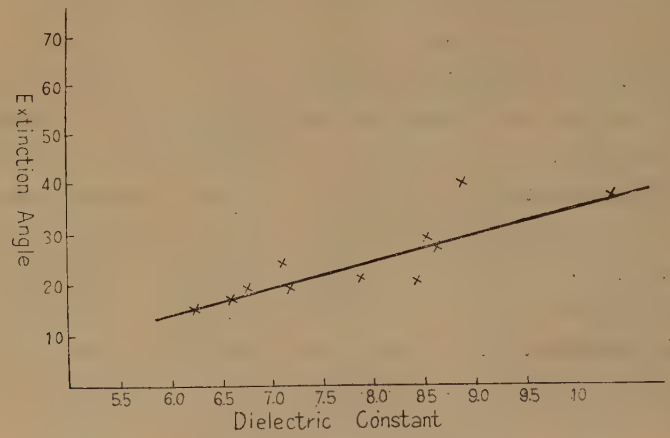


Fig. 8. Relationship between dielectric constant and extinction angle of amphibole.

## *Résumé*

(1) The dielectric phenomena of minerals are derived from the atomic and electronic polarizations and with some minerals orientational polarizations arise on an adequate magnetic frequency wave. No remarkable difference can be recognized between the two dielectric constants which were measured with ultra short wave having the wave length 101.43 cm. and with intermediate wave having 500 kc. with the exceptions of hydrated minerals such as opal and agate.

(2) A relationship between the dielectric constants and An contents of plagioclases can be shown by the experimental formula, $\varepsilon=5.473\ (\pm0.016)+0.00241\ (\pm0.00010)\ An-0.000070\ (\pm0.000010)\ An^2$. From this formula, the An contents of plagioclase may be obtained by determing the dielectric constant.

(3) The component of $MgSiO_3$ is so related to the dielectric constant of pyroxene mineral as the decrease of its contents inverse proportionally increase the constant. The $CaSiO_3$ and $FeSiO_3$ components show almost no different influence on the dielectric constants.

(4) The tremolite-actinolite series which contain relatively small amount of $R_2^{III}O_3$ and CaO component, increase their dielectric constants according to the increase of FeO or decrease of MgO component as like the pyroxene minerals. On the other hand, some varieties of amphiboles, containing a large amount of $R_2^{III}O_3$ components, show no regular relationship between the dielectric constants and merely $R^{II}O$ components, while a regularity between the components MgO, (Ca, Fe) O, $(Al, Fe)_2 O_3$ and dielectric constants was found.

(5) The extinction angles are also intimately related to the dielectric constants of these minerals. The increase of extinction angle is followed by its high dielectric constant.

(6) The dielectric constants of minerals change their values according to the chemical constitutions and crystal structures. So it was an important problem to solve the close relations between the chemical compositions and dielectric constants of isomorphous minerals.

The present writers have been encouraged to promote this new research in the mineralogy.

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# ON THE DIELECTRIC CONSTANTS OF ROCKS

## (The Determination of Dielectric Constants of Minerals and Rocks and their Applications to the Mineralogical[8)11)] and Geological Studies, Part 2)

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### *Preface*

The present writers have previously proposed[9)] a new way of correlating the stratification of the sedimentary rock series by means of comparing the dielectric constants of rocks belonging to one stratified series with those belonging to the others to be correlated.

W. O. George[3)] has studied the relationship between the chemical compositions of the eruptive rocks and the refractive indices of their natural glasses and later, W. H. Mathews[4)] and A. Harker has carried out the study to which the silica-contents of igneous rocks and refractive indices of artificially fused glasses of those rocks are related. If the material of metallic crystal is subjected to the electronic polarization effect, its dielectric constant is given as the square of the refractive index according to the Maxwell's electromagnetic theory[2)]. In the case of ionic-crystal mineral[1)10)], however, the dielectric constant is greater than that expected by Maxwell's theory owing to the other adjoining polarizations such as the atomic or in rare case, orientational[12)] polarization effect. Though the fact is so, the variation of the dielectric constant determined by the ultra short electromagnetic wave should show the same manner as that of refractive index providing nearly the same effect of atomic polarization on the dielectric constant.

The dielectric constants determined by pulverized powder sample

of igneous rock may be considered as the mean dielectric constants[2] of respective rock forming minerals, taking account of their volumetric proportions.

According to the studies on the relationships between the chemical compositions and dielectric constants of numerous silicate[8][11] minerals of which the various igneous rocks are consisted, following mineral associations may be considered that the minerals of high dielectric constant quite likely associate with the members which have relatively high dielectric constants and low dielectric constant minerals with relatively low members. According to these facts, the dielectric behaviours of igneous rocks are naturally attributed to their mineral associations.

Upon the standpoint of this view, the authors have attempted the experiments in order to determine the relationship between the silica-contents and the dielectric constants of igneous rocks suitably pulverized for our experiment.

### *The relationship between the dielectric constants and silica-contents of the igneous rocks.*

Of the various kinds of igneous rocks, the dielectric constants were measured by the immersion method employing the ultra short electromagnetic wave and at the same time, the silica contents were analytically determined. The results are summarized in Table 1 and the relationship between the dielectric constants and the silica-contents is diagrammatically expressed in Fig. 1. The latter holds the same meaning comparing with the result which was demonstrated by W. H. Mathews on the relationship between the index of refraction and silica-content as shown in Fig. 2.

As we expected from the previous reports, the dielectric constant gradually rises with the decrease of the silica-content, the dielectric constant of acidic rock being 4.9 to 5.1 and that of basic rock, 7.0 to 7.5.

Table 1

| Nominated Rock | Locality | Dielectric Const. | $SiO_2$% | $H_2O$% | No. of Specimen |
|---|---|---|---|---|---|
| (1) Granite-Group | | | | | |
| Granite | Nose, Ōsaka | 4.95 | 75.76 | 0.14 | 1 |
| Granite | Kitashirakawa | 5.00 | 70.46 | 0.28 | 2 |
| Hornblende Granite | Ibaragi | 4.95 | 69.06 | 0.39 | 3 |
| (2) Granite Porphyry-Group | | | | | |
| Granite Porphyry | Sakamoto, Shiga | 4.90 | 76.91 | 0.36 | 4 |
| Granite Porphyry | Yawatahama | 4.95 | 73.97 | 0.33 | 5 |
| Granite Porphyry | Mottpo Korea | 4.95 | 72.84 | 1.46 | 6 |
| (3) Liparite-Group | | | | | |
| Liparite | Tonan Island | 5.05 | 73.68 | 5.05 | 7 |
| Liparite | Yarai, Hyogo | 5.10 | 68.64 | 5.10 | 8 |
| (4) Diorite-Group | | | | | |
| Monzonite | Yakuoji | 5.55 | 62.44 | 0.45 | 9 |
| Diorite | Ryumondake | 7.45 | 49.84 | 0.29 | 10 |
| Diorite | Genjigamine | 7.25 | 49 36 | 0.40 | 11 |
| Diorite | Maizuru, Kyoto | 7.53 | 49.30 | 0.50 | 12 |
| Diorite | Ayabe, Kyoto | 7.35 | 48.69 | 0.58 | 13 |
| (5) Porphyrite-Group | | | | | |
| Porphyrite | Ōro, Kyoto | 6.08 | 56.03 | 1.33 | 14 |
| Porphyrite | Kitashirakawa | 7.10 | 48.88 | 0.46 | 15 |
| (6) Andesite-Group | | | | | |
| Andesite | Tsuyama | 5.75 | 62.39 | 0.27 | 16 |
| Andesite | Azumayama | 5.90 | 61.16 | 0.62 | 17 |
| (7) Gabbro-Group | | | | | |
| Gabbro | Murotozaki | 7.10 | 50.94 | 0.26 | 18 |
| (8) Diabase-Group | | | | | |
| Diabase | Shionomisaki | 7.05 | 49.49 | 0.26 | 19 |
| Diabase | Kuramayama | 7.50 | 45.72 | 0.73 | 20 |
| (9) Basalt-Group | | | | | |
| Basalt | Genbudo | 7.30 | 48.95 | 0.24 | 21 |
| Basalt | Takurayama | 7.05 | 48.68 | 0.58 | 22 |
| Basalt (meranocratic) | Genbudo | 8.60 | 45.42 | 0.47 | 23 |

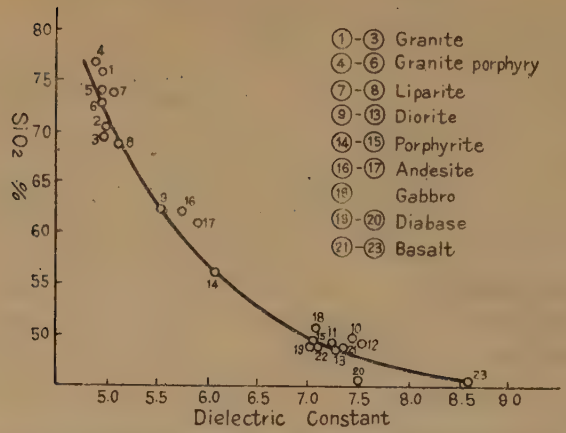


Fig. 1. D. C.-$SiO_2$ content diagram of various igneous rocks.

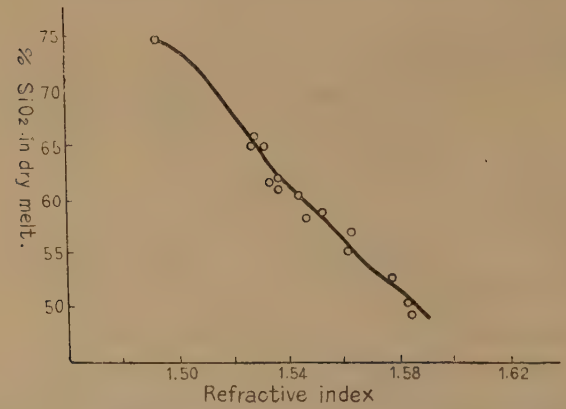


Fig. 2. R. I.-$SiO_2$ content diagram of Quaternary volcanic rocks.

According to the result obtained by W. O. George and M. Stark,[7] there is the difference as much as 14% of silica-content among the rocks having the same refractive index and conversely say, there is the difference as much as 0.065 of refractive index among the rocks having the same content of silica.

Such a discrepancy may be ascribed to the fact that the sample usually encountered in the field is not wholly glassy but contain some crystalline materials in it.

*The dielectric constants of eruptive rocks distributed in the area of Aso-caldera.*[5)6)]

There are numerous dominating volcanic cones in the great Aso-caldera and each of them is also accompanied with several parasitic cones. A number of specimens of lavas were collected from all points of area, whose located points are plotted in the following geological map of Aso-caldera shown in Fig. 3.

With these specimens, the dielectric constants and the contents of silica were respectively determined (Table 2). In the same way, the relation of the dielectric constant and the content of silica is expressed in the following Fig. 4.

Some deviated points from the normal curve may be ascribed to the partially weathered rock specimens.

Judging from the field informations on the distributions of lavas and the determinations of the dielectric constants of those lavas, we can point out the following facts concerning the chemical characters of the repeatedly erupted lavas.

(1) The volcanic activity in this area had commenced with the eruption of acidic lava from the Senrigahama-crator. This lava ($S_3$) was extensively spread over the area west of Kurokawa and its mean dielectric constant is measured as 5.76. Following this, the eruptions of the lava $S_2$ (D. C. 6.83) and $S_1$ (D. C. 5.90) were repeated from the same crator. Those lavas covered the south western part of the caldera.

Several parasitic cones were built during this period and the dielectric constants of their lavas are measured as 5.61 (Kenkyusho-yama), 5.95 (Janoo-yama), 6.13 (Okamado-yama), 6.17 (Yunotani-yama) etc.

(2) The center of the volcanic activity removed to the eastern Naka-dake region and its remnants are found as Nara-yama (D. C. 6.52) lying on the base of the Naka-dake.

After these volcanic actions, the plentifull intermediate lavas

Fig. 3. Geological map of the Aso-Caldera.

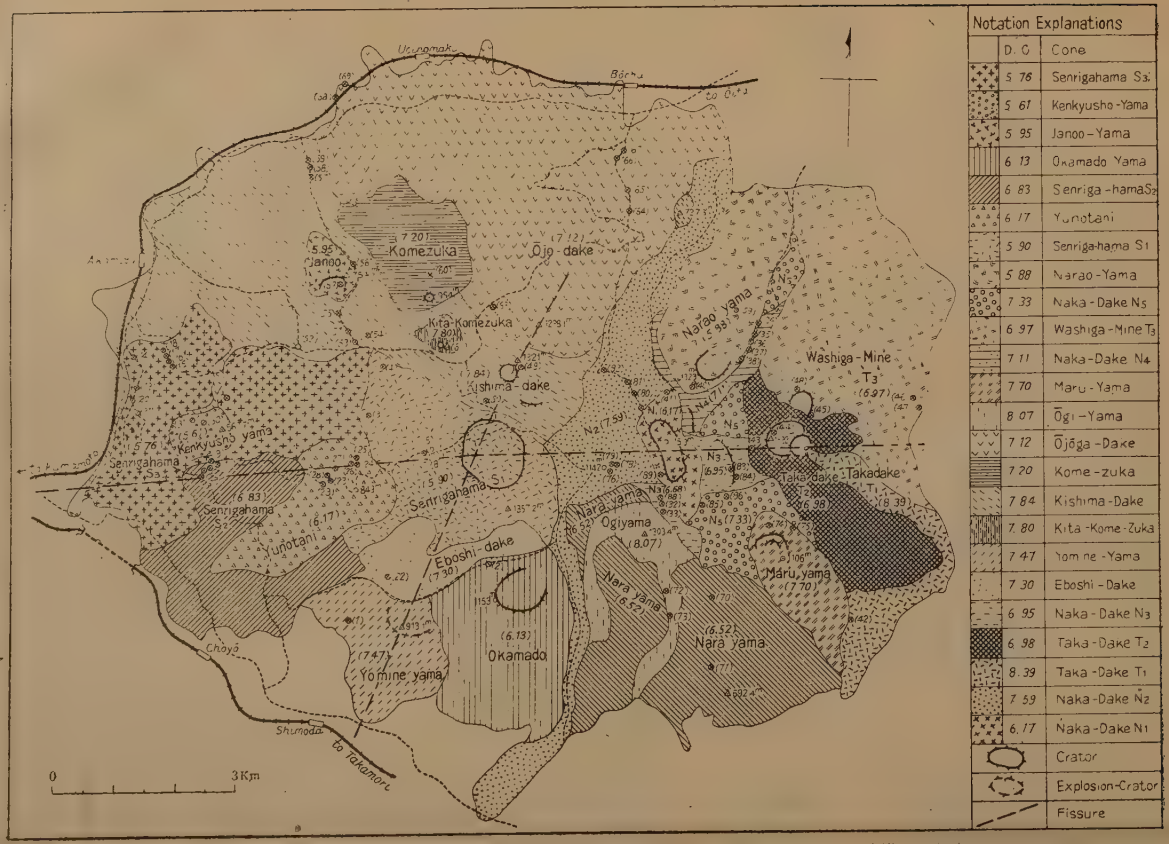

Table 2

| Cone | No. | D. C. | $SiO_2$ | | Cone | No. | D. C. | $SiO_2$ | |
|---|---|---|---|---|---|---|---|---|---|
| Yomine-yama | 1 | 7.47 | 52.64 | | | 52 | 8.33 | 52.07 | |
| Okamado-yama | 2 | 6.13 | 60.98 | | | 53 | 7.21 | | |
| Senrigahama | 3 | 6.25 | 66.73 | $S_1$ | | 54 | 7.45 | | |
| | 5 | 5.35 | | $S_1$ | | 55 | 8.75 | 50.24 | |
| | 6 | 5.20 | 66.42 | $S_1$ | | 56 | 8.05 | 52.08 | |
| | 7 | 5.77 | | $S_1$ | | 57 | 7.20 | | |
| | 8 | 5.99 | | $S_1$ | | 58 | 6.50 | | |
| | 9 | 7.20 | 57.42 | $S_2$ | | 59 | 6 95 | | |
| | 10 | 6.18 | | $S_2$ | Kometsuka | 60 | 7.20 | | |
| | 11 | 6.65 | 58.99 | $S_2$ | Kita-kometsuka | 61 | 7.80 | 50.65 | |
| | 12 | 7.65 | | $S_2$ | Janoo | 62 | 5.95 | | |
| | 13 | 6.45 | 59.03 | $S_2$ | Ōjōga-dake | 63 | 7.53 | | |
| | 14 | 5.70 | 65.99 | $S_3$ | | 64 | 7.95 | 51.22 | |
| | 15 | 5.75 | | $S_3$ | | 65 | 7.13 | | |
| | 16 | 6.03 | 66.33 | $S_3$ | | 66 | 7.00 | | |
| | 17 | 5 43 | | $S_3$ | | 67 | 6.95 | | |
| | 18 | 5.70 | 66.05 | $S_3$ | Ōgi-yama | 72 | 7.75 | 51.93 | |
| | 19 | 5.81 | | $S_3$ | | 73 | 8.38 | 52.17 | |
| | 20 | 5.80 | | $S_3$ | Maru-yama | 74 | 7.65 | 54.11 | |
| | 21 | 5.80 | | $S_3$ | | 75 | 7.75 | | |
| Eboshi-dake | 22 | 7.30 | 57.30 | | Naka-dake | 41 | 6.23 | | $N_1$ |
| Yunotani | 23 | 6.00 | 57 30 | | | 88 | 6.05 | 58.79 | $N_1$ |
| | 24 | 5.95 | | | | 89 | 6.23 | | $N_1$ |
| | 25 | 6 34 | | | | 76 | 7.78 | 53.26 | $N_2$ |
| | 26 | 6.30 | 64 83 | | | 78 | 7.10 | | $N_2$ |
| | 27 | 6.20 | | | | 79 | 7.60 | 50.59 | $N_2$ |
| | 28 | 6.31 | 66.31 | | | 80 | 7.95 | | $N_2$ |
| | 29 | 6.15 | | | | 81 | 7.50 | 52.06 | $N_2$ |
| Kenkyusho-yama | 30 | 5.80 | 72.66 | | | 82 | 6.40 | | $N_2$ |
| | 31 | 5.41 | 71.18 | | | 83 | 6.40 | | $N_3$ |
| Narao-yama | 39 | 5.80 | | | | 84 | 6.95 | | $N_3$ |
| | 40 | 5.95 | 58.77 | | | 32 | 7.00 | 58.28 | $N_3$ |
| Taka-dake | 42 | 8.39 | | $T_1$ | | 33 | 7.40 | 54.07 | $N_3$ |
| | 43 | 7.00 | | $T_2$ | | 34 | 6.68 | | $N_4$ |
| | 44 | 6.95 | | $T_2$ | | 35 | 7.30 | | $N_4$ |
| | 45 | 6.80 | | $T_3$ | | 36 | 6.75 | | $N_4$ |
| | 46 | 6.78 | | $T_3$ | | 37 | 7.40 | | $N_4$ |
| | 47 | 6.84 | | $T_3$ | | 38 | 7.40 | | $N_4$ |
| | 48 | 7.47 | 54.00 | $T_3$ | | 85 | 7.00 | 52.98 | $N_5$ |
| Kishima-dake | 49 | 8.10 | | | | 86 | 7.65 | 51.28 | $N_5$ |
| | 50 | 7.50 | | | Nara-yama | 70 | 6.23 | | |
| | 51 | 7.58 | 50.76 | | | 71 | 6.80 | 58.36 | |

$N_1$, $N_2$, $N_3$ etc. respectively show the differenciated lavas which flowed out from the Naka-dake crator.

spread over the north-eastern part of the caldera forming the Narao-dake (D. C. 5.88) and Washigamine $T_3$ (D. C. 6.97). This activity period may be characterised by the eruptions of intermediate lavas.

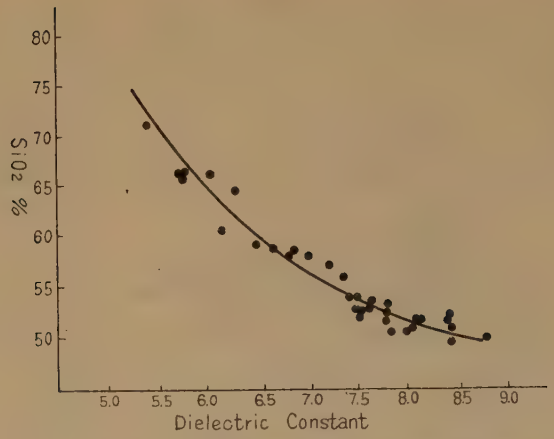


Fig. 4. D. C.-$SiO_2$ content diagram of the Aso volcanic lavas.

(3) The activity of the Naka-dake is going on now forming the Naka-dake peak $N_5$ (D. C. 7.33), which is accompanying the parasitic cones such as the Maru-yama (D. C. 7.70) and Ĉgi-yama (D. C. 8.07) consisted of more basic lavas.

From this time, the active center was removed to the NE-SW structural fissure at the Senrigahama and constructed the principal members of so called "Aso Five Peaks" such as Ōjōga-dake (D. C. 7.12), Kishima-dake (D. C. 7.84), Yomine-yama (D. C. 7.47) and Eboshi-dake (D. C. 7.30). Then the volcanic activity changed its center to the Naka-dake forming the high rock-wall on the eastern side of the Sunasenri with the Sara-yama $N_3$ (D. C. 6.95).

Then the Taka-dake eruption $T_2$ (D. C. 6.98) began accompanying a new lava flow $T_1$ (D. C. 8.39) which flowed down toward the south-eastern side. The Taka-dake is now under active condition emissioning a large volume of sulphurous gas emanations from the central crator after the eruptions of significant quantities of two lavas $N_2$ (D. C. 7.59), $N_1$ (D. C. 6.17). This eruption stage should be considered as a basic lava stage.

The variation diagram of the dielectric constants of the lavas erupted from these cones may be shown as Fig. 5 considering the above described eruption sequences.

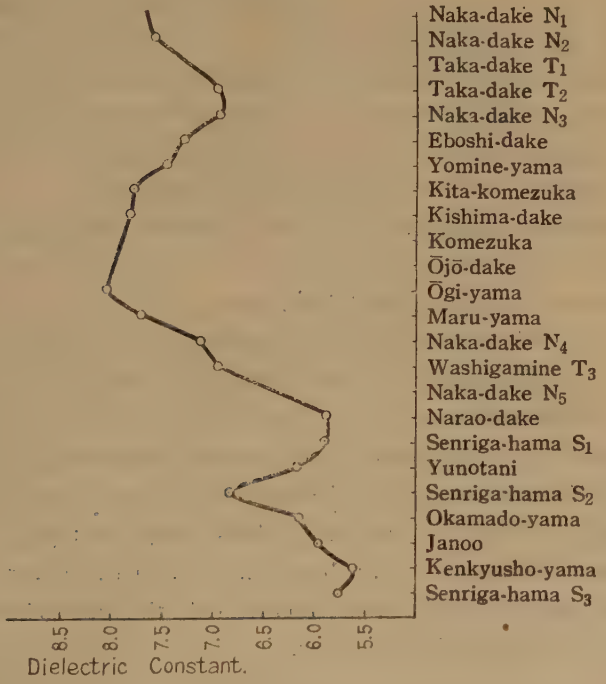


Fig. 5. D. C. variation diagram of numerous volcanic cones.

Judging from this diagram, it is noticeable that the general tendency of the dielectric constants increases their values with the exceptions of two decreasing stages.

These facts indicate the general decrease of silica-contents with the exceptions of increasing their acidities at the eruptions of the Senrigahama $S_2$ lava and Ōgiyama lava.

## *Résumé*

(1) The classification of igneous rocks by the dielectric constant is easily accomplished by the direct determination of the total die-

lectric constant of rock-powder using a little specimen about 0.5 grm. A relatively smooth curve relating the silica-content and dielectric constant of igneous rocks was obtained.

(2) In the case of silica content and refractive index diagram of natural glassy rock, the refractive indices of phenocrysts should be neglected and of fused glass of rock, the significant changes such as the loss of volatile constituents, oxidation of iron, extraction of some composition from the vessel should be brought about in the chemical composition during the artificial melting.

Therefore the refractive index thus obtained does not show the specific character of the original rock. On the contrary, this method will eliminate these significant influences.

(3) The dielectric constants of lavas erupted from the numerous cones or parasitic cones in the Aso-caldela were determined and the relationship to their silica-contents was shown diagrammatically. On the other hand, the eruption sequence of each cone was clarified as follows by considering the distributions of rocks and the results of dielectric constants. The acidic lavas were erupted from the older cones, while the more basic lavas than them were erupted from the comparatively younger cones with the exceptions of two stages which increased the acidity.

*Acknowledgements*

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# THE DIFFERENTIAL THERMAL ANALYSIS CURVES AND THE DEHYDRATION CURVES OF ZEOLITES*

## (Studies on Water in Minerals, Part 1)

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ABSTRACT

Dehydration curves and differential thermal analysis curves of several different kinds of zeolites are presented here and discussed with reference to their dehydration phenomena. The zeolites include ptilolite, heulandite, epistilbite, stilbite, laumontite, chabazite, analcime, natrolite, scolecite, mesolite and thomsonite. And it was revealed that there are some types of dehydration phenomena. These types are: (1) Natrolite type showing sharp dehydration phenomena in which water of crystallization is entirely lost.···Natrolite. (2) Analcime type showing smooth dehydration phenomena.···Ptilolite, chabazite and analcime. (3) The combined type of the two above mentioned.···Heulandite, laumontite, scolecite and mesolite. (4) The type which does not belong to any of the two types.··· Epistilbite, stilbite and thomsonite.

### *Introduction*

Zeolites having characteristic water of crystallization, which is called as "zeolitic water", and showing remarkable base exchange, are the most interesting one of many hydrous minerals. And, many studies on zeolites have been already carried out by chemists and mineralogists, but these studies are imperfect with many questions still undisolved. In this paper, a preliminary report of reexamining studies on zeolite is given in which dehydration curves and differen-

* The experiments had been carried out at Geological and Mineralogical Institute, Kyoto University, from 1946 to 1950. Read at the 57th Annual Meeting of the Geological Society of Japan held in Tokyo on April 7, 1950.

tial thermal analysis (DTA will be used below as the simple form for the differential thermal analysis.) curves of many varieties of zeolite are included, and also the present writer's view on the dehydration phenomena are given.

### *Samples and their chemical composition*

Twenty-three specimens were used in the experiments as tabulated in Table 1.

The identification of these specimens were done by these chemical composition, crystal morphology, optical properties and etc.. Eighteen of these specimens, have been identified by chemical analysis, and the following results were obtained (Table 2).

### *Loss of weight and differential thermal analysis*

By the measurements of loss in weight and DTA, the dehydration phenomena of zeolites were examined. The apparatus used to measure the loss of weight is the Ôshima-Fukuda's thermobalance. Each specimen ground to fine powder (0.3 gr. in thermobalance and 2.0 gr. in DTA) was used for experiments. In DTA, the rate of heating was 2–3°C. per minute. Of thermobalance, the heating was carried out step by step. That is, temperature was raised by 20°C. to the next step, and at each step of temperature the weight of specimen had been kept to be constant 2 minutes. The results of experiments are partly shown diagrammatically in Figs. 1, 2 and 3. The characters of dehydration phenomena of each zeolite will be discussed below.

*Ptilolite.* According to the experiments carried out by the author, the largest part of water in ptilolite is lost slowly below 500°C., and the remainder is perfectly removed at 700°C., showing the DTA curve of slow endothermic reaction. Generally, dehydrated zeolites after heating at 800°C., except ptilolite and chabazite, scarcely rehydrate when they were left as it was in air. On the contrary,

Table 1

| Sample No. | Name of mineral | Locality |
|---|---|---|
| 24 | Ptilolite | Nakano, Nakagawa-mura, Fukui Pref., Japan |
| 31 | Ptilolite | Sotoura, Hamazaki-mura, Shizuoka Pref., Japan |
| 21 | Heulandite | Chichi-Shima, Ogasawara Islands |
| 38 | Epistilbite[1] | Yugawara, Kanagawa Pref., Japan |
| 2 | Stilbite* | Teigarhorn, Iceland |
| 4 | Stilbite** | Weiz, Fellital, Schweiz |
| 39 | Stilbite[1] | Yugawara, Kanagawa Pref., Japan |
| 10 | Laumontite | Plauenscher Grund, Sachsen |
| 33 | Laumontite | Yugawara, Kanagawa Pref., Japan |
| 34 | Laumontite | Ashio Mine, Tochigi Pref., Japan |
| 35 | Laumontite | Shuzenzi, Shizuoka Pref., Japan |
| 5 | Chabazite | Oberstein, a. d. Nahe, Rhein Prov. |
| 42 | Chabazite*** | Mitaki, Sendai, Japan |
| 6 | Analcime | Seis, Tirol |
| 9 | Natrolite**** | Uri, Schweiz |
| 3 | Scolecite | Teigarhorn, Iceland |
| 19 | Scolecite | Teigarhorn, Iceland |
| 14 | Mesolite | Nishishioda-mura, Nagano Pref., Japan |
| 15 | Mesolite | Nishishioda-mura, Nagano Pref., Japan |
| 18 | Mesolite | Kilpatrick, Dumbertonschier, (nr. Glasgow) Scottland |
| 40 | Thomsonite | Maze, Niigata Pref., Japan |
| 41 | Thomsonite | Table Mountain, Golden, Colorado, North America |
| 1 | Apophyllite***** | Kamioka Mine, Gifu Pref., Japan |

* This specimen had been misnamed "Heulandite" by the collector.

** This specimen had been named "Desmin" by the collector.

*** This specimen had been misnamed "Gmelinite" by the collector.

**** This specimen had been misnamed "Stilbite" by the collector. The dehydration phenomena of the zeolite with intermediate chemical composition between natrolite and mesolite are described in Part 2 of this studies.[6]

***** Apophyllite which does not belong to zeolites, was also used in experiments.

Table 2

| Sample No. | Name of mineral | Chemical composition (weight %) | | | | | | Molecular ratio | | | | | Analyst |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | $Al_2O_3$ | CaO | $Na_2O$ | I. L. | Total | $SiO_2$ | $Al_2O_3$ | CaO | $Na_2O$ | $H_2O$ | |
| | | % | % | % | % | % | % | | | | | | |
| 38 | Epistilbite | 56.26 | 17.78 | 8.77 | 2.17 | 15.86 | 100.84 | 5 | 1 | 1 | | 5 | HAYASHI[1] |
| 2 | Stilbite | 57.32 | 16.03 | 7.85 | 0.96 | 18.85 | 101.19 | 6 | 1 | 1 | ... | 6.5 | KOIZUMI |
| | | | | | $K_2O = 0.18$ | | | | | | | | |
| 4 | Stilbite | 56.76 | 16.37 | 7.84 | 1.50 | 18.80 | 101.27 | 6 | 1 | 1 | | 6.5 | KOIZUMI |
| 39 | Stilbite | 56.50 | 18.62 | 7.33 | 1.31 | 18.71 | 100.79 | 5 | 1 | 1 | | 6 | HAYASHI[1] |
| | | $Fe_2O_3$ = tr., FeO = none, $K_2O = 0.12$ | | | | | | | | | | (including $K_2O$) | |
| 10 | Laumontite | 49.45 | 24.18 | 10.97 | ... | 15.39 | 99.99 | 3.5 | 1 | 1 | ... | 3.5 | KOIZUMI |
| 33 | Laumontite | 53.82 | 20.85 | 11.41 | ... | 14.77 | 100.85 | 4 | 1 | 1 | ... | 4 | KOIZUMI |
| 34 | Laumontite | 52.83 | 20.72 | 11.52 | ... | 14.45 | 99.52 | 4 | 1 | 1 | ... | 4.5 | KOIZUMI |
| 35 | Laumontite | 52.30 | 21.52 | 11.76 | ... | 14.40 | 99.98 | 4 | 1 | 1 | ... | 4 | KOIZUMI |
| 42 | Chabazite | 47.44 | 20.20 | 10.09 | 1.34 | 21.00 | 100.67 | 4 | 1 | 1 | | 6 | KOIZUMI |
| 9 | Natrolite | 46.10 | 28.12 | 1.55 | 13.41 | 10.70 | 99.88 | 3 | 1 | 1 | | 2 | KOIZUMI |
| 3 | Scolecite | 47.08 | 25.16 | 14.59 | ... | 13.40 | 100.23 | 3 | 1 | 1 | ... | 3 | KOIZUMI |
| 19 | Scolecite | 45.71 | 26.87 | 14.08 | ... | 13.88 | 100.54 | 3 | 1 | 1 | ... | 3 | KOIZUMI |
| 14 | Mesolite | 45.70 | 27.16 | 9.67 | 4.24 | 13.36 | 100.13 | 9 | 3 | 2 | 1 | 8 | KOIZUMI |
| 15 | Mesolite | 45.97 | 27.00 | 10.10 | 4.98 | 12.78 | 100.83 | 9 | 3 | 2 | 1 | 8 | KOIZUMI |
| 18 | Mesolite | 45.66 | 26.11 | 10.90 | 4.46 | 13.53 | 100.66 | 9 | 3 | 2 | 1 | 9 | KOIZUMI |
| 40 | Thomsonite | 36.94 | 32.47 | 12.92 | 5.18 | 13.50 | 100.98 | 2 | 1 | 1 | | 2.5 | HAYASHI |
| | | MgO = tr., $K_2O$ = none | | | | | | | | | | | |
| 41 | Thomsonite | 41.47 | 28.86 | 10.82 | 5.05 | 15.02 | 101.22 | 2.5 | 1 | 1 | | 3 | KOIZUMI |
| 1 | Apophyllite | 52.03 | 0.00 | 25.64 | 0.65 | 16.77 | 100.41 | 16 | 0 | 8 | 1 | 17 | KOIZUMI |
| | | $Fe_2O_3 = 0.29$, MgO = tr., $K_2O = 5.03$ | | | | | | | | | $K_2O$ | | |

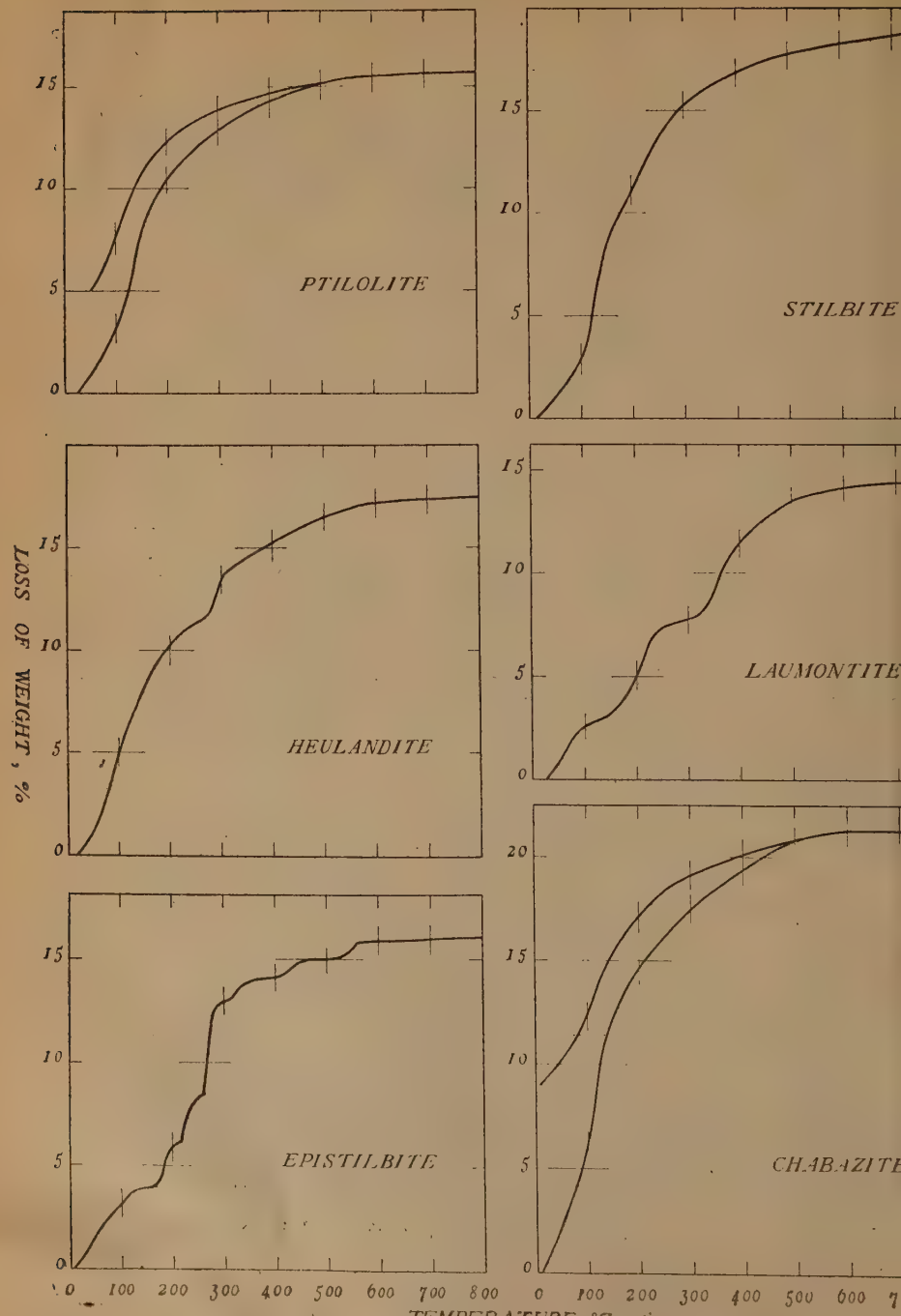


Fig. 1. The dehydration curves of zeolites (Part 1).

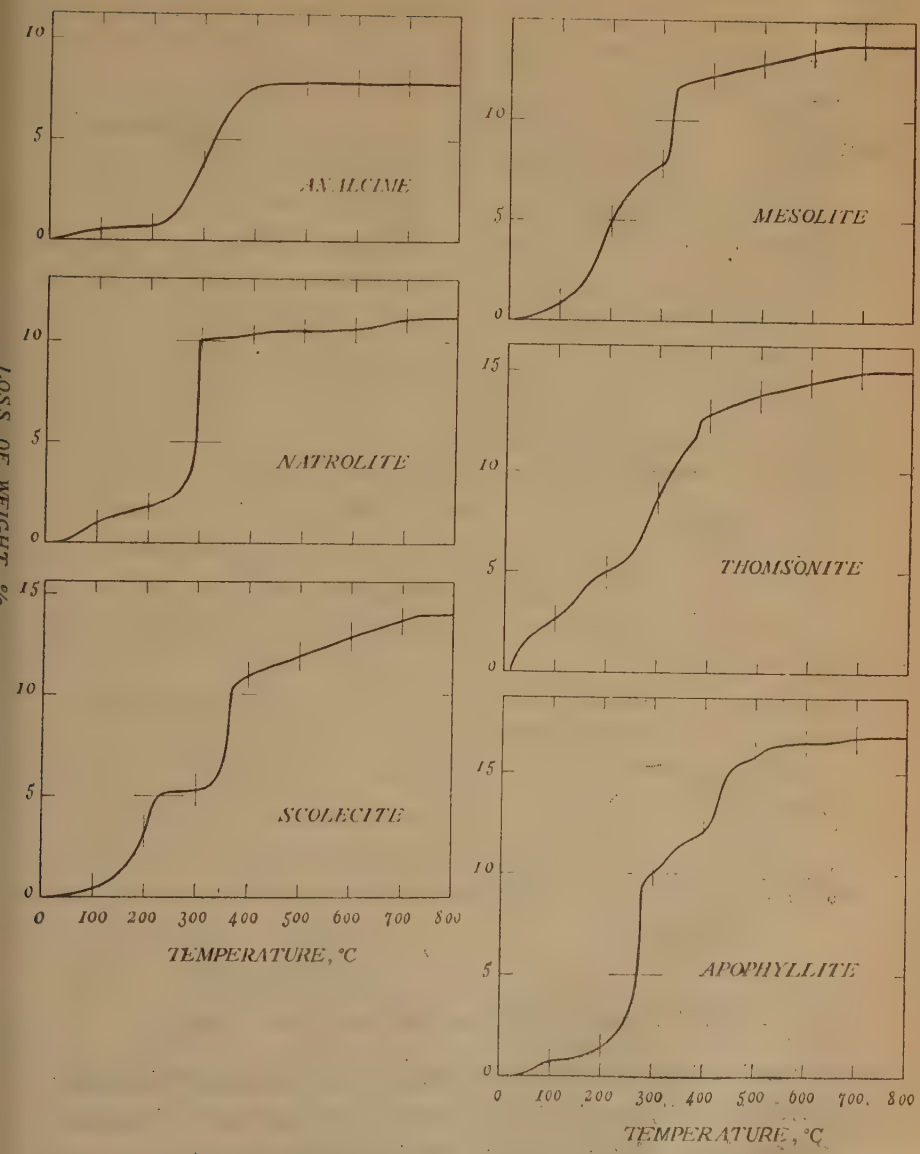


Fig. 2. The dehydration curves of zeolites (Part 2).

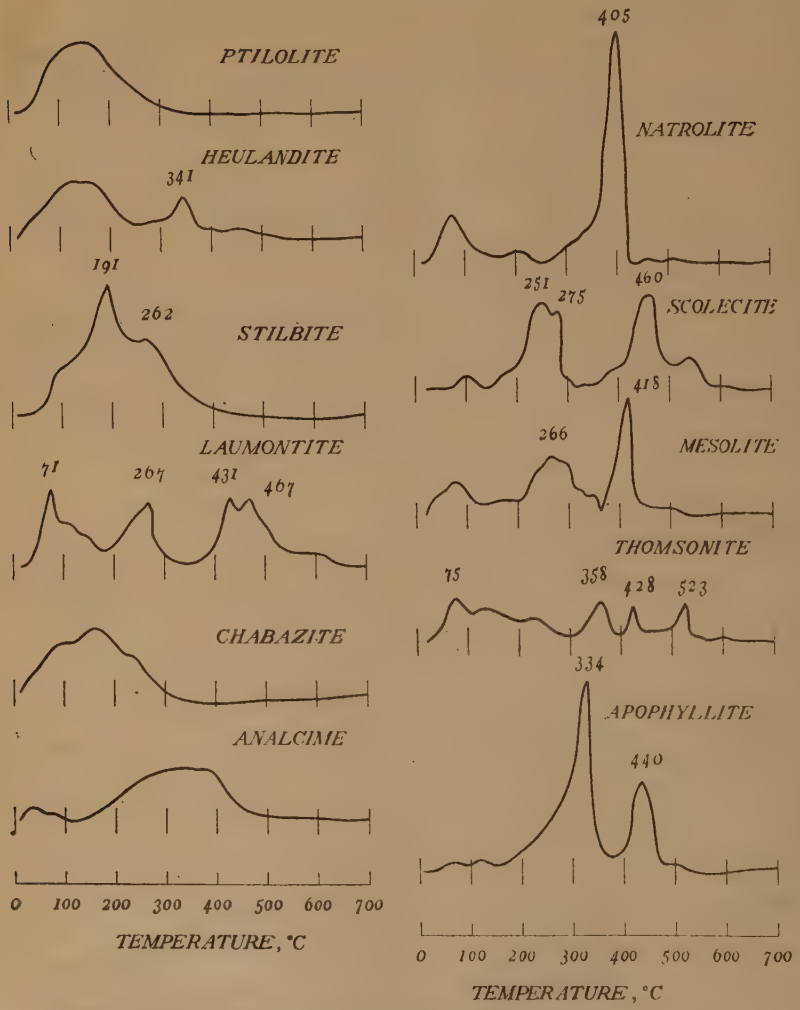


Fig. 3. The differential thermal analysis curves of zeolites.

dehydrated ptilolite and chabazite have a very characteristic ability to rehydrate easily again in air. Rehydrated specimens dehydrate as it was before by reheating. In Fig. 1, the upper of the two curves of ptilolite is the dehydration curve of rehydrated ptilolite which was let alone in air 14 hours after heating at 800°C. and the

lower is that of the original specimen.

*Heulandite.* About 65% of water in this specimen (This corresponds to about 3 molecules of water) is lost continuously below ca. 260°C., and subsequently a part of the remainder dehydrates rapidly at 280°C., and then the rest does slowly to 600°C.. The DTA curve of this specimen shows the slow endothermic change between the room temperature and 260°C. and rather sharp endothermic peak at 341°C.. It is interesting that heulandite with a sharp dehydration phenomenon at 280°C. which is not found in stilbite, shows the different dehydration phenomena from stilbite with the remarkable endothermic peak at 191°C. which is lacking in heulandite, whereas the former is similar to the latter in their mineralogical properties and in the content of water of crystallization. Studies on the dehydration phenomena of heulandite had been carried out by Kôzu and Masuda[3] and by Milligan and Weiser[5]. These results are not coincident with that of the present author. On the dehydration phenomena of this specimen, more detailed investigation will be needed.

*Epistilbite.* As it was difficult to obtain enough of amount of this specimen, the DTA curve was not obtained but only the dehydration curve was given. As shown in Fig. 1, the curve shows the complex stepwise dehydration phenomena. It is interesting that epistilbite shows the different dehydration phenomena from heulandite and stilbite, whereas these three zeolites have similar chemical compositions.

*Stilbite.* While the curve showing loss of weight is rather similar to that of heulandite and chabazite, the DTA curve is characterized by the endothermic peaks at 191°C. and 262°C.. Studies on the dehydration phenomena of stilbite had been carried out by Milligan and Weiser[5]. The result by them is approximately similar to that of the present author.

*Laumontite.* Laumontite dehydrates in three stpes, between the room temperature and 150°C., between 150°C. and 300°C. and between

300°C. and 700°C.. The dehydration in each step is slow and gradual. Three endothermic peaks at 71°C., 267°C. and 431~467°C. in DTA curve are corresponding to the dehydration in each step. Studies on the dehydration phenomena of laumontite have never been carried out.

*Chabazite.* This specimen is approximately similar to ptilolite in the dehydration and rehydration phenomena except that the content of water in this specimen is larger than that of ptilolite. In Fig. 1, the upper of the two curves of chabazite shows the dehydration curve of rehydrated chabazite let alone in air 47 hours after heating and the lower is that of the original specimen.

*Analcime.* Analcime dehydrates so slowly and gradually between 200°C. and 400°C. that in DTA curve only a slow endothermic curve is obtained without a sharp endothermic peak. There is no difference between the results by Milligan and Weiser[5] and that of the present author.

*Natrolite.* In strict sense of nomenclature, this specimen cannot be called natrolite, because it contains about 1.55% of CaO. The most of water is lost suddenly at 300°C. corresponding to the endothermic peak at 405°C. in DTA curve. W. O. Milligan and H. B. Weiser[5] had found that natrolite changed to monohydrate with the beginning of dehydration at 160°C. and to anhydrous at 350°C.. Points of contrast between the results obtained by them and ones by the writer are noticed. The dehydration phenomena of natrolite shown by them is rather approximate to that of mesolite obtained by the writer. The difference of the results above mentioned is likely to be dependent on the purity of specimens.

*Scolecite.* Most part of water of crystallization in this material is removed rapidly in two steps at 200°C. and 370°C., and subsequently the remainder is dehydrated continuously in the range of temperature between 400°C. and 750°C.. Correspondingly to the sharp dehydrations in two steps above mentioned, there are two remarkable endothermic peaks at 251°C. and 460°C. in DTA curves. The

phenomenon that the endothermic peak corresponding to the dehydration at first step differentiates strictly into two peaks at 251°C. and 275°C. in every specimens, is seemed to be interesting and significant. The data of scolecite obtained by the author are in accordance with that by Milligan and Weiser[5].

*Mesolite.* The half amount of water in this specimen is lost slowly below 300°C., and subsequently one-third rapidly at 330°C., and then the remainder dehydrates slowly below 650°C.. The DTA curve of this specimen shows a comparatively slow endothermic change between 266°C. and 292°C. and a very sharp endothermic peak at 418°C.. It is interesting that mesolite dehydrated below 300°C. has the ability to absorb the moisture in air. Consequently, it seems that the mechanism of dehydration of mesolite below 300°C. is similar to that of chabazite and ptilolite. The results mentioned above is nearly in accordance with that by Milligan and Weiser[5].

*Thomsonite.* The dehydration curve of this specimen is rather similar to that of natrolite. Strictly speaking, however, it shows its proper dehydration phenomena, that is, it dehydrates very slowly below 250°C., and later rapidly in the range of temperature up to 380°C.. Four endothermic peaks at 75°C., 358°C., 428°C. and 523°C. found in DTA curves, is corresponding to the dehydration above mentioned. Hey and Bannister[2] had obtained a continuous dehydration isobar for the usual variety of thomsonite, but observed a break in the isobar for a special sample. The results obtained by the writer for two specimens of thomsonite belong to the latter case.

*Apophyllite.* Apophyllite dehydrates in two steps, that is, rapidly at 280°C. and rather slowly between 280°C. and 440°C.. The sharp endothermic peaks at 334°C. and 440°C. in DTA curves show the dehydration to proceed in two steps. The results above mentioned are in accordance with that obtained by Kôzu, Yagi and Jizaimaru[4].

*Summary and conclusion*

From the studies on dehydration and DTA curves of the many varieties of zeolites, it is confirmed that the zeolites are classified into the following some types according to their dehydration phenomena.

(1) *Natrolite type.* Minerals of this type lost their water of crystallization entirely at short intervals of temperature. The endothermic peak in DTA, corresponding to the rapid dehydration, is very sharp. Natrolite belongs to this type.

(2) *Analcime type.* The dehydration of minerals of this type does not proceed stepwise but gradually. It is probably due to the so called "zeolitic water". Ptilolite, chabazite and analcime are classified into this type. Zeolites having a strong ability of rehydration, such as chabazite and ptilolite, show the dehydration phenomena of this type.

(3) *The combined type of the two above mentioned.* The dehydration phenomena of this type is different from either of the two mentioned above, but seems to be partly the combination of the two types. Heulandite, laumontite, scolecite, mesolite and apophyllite belong to this type.

Heulandite: The smooth dehydration process of heulandite below ca. 260°C. is similar to the analcime type, and the rapid dehydration at 280°C., the natrolite type.

Laumontite: The dehydration process of laumontite is seemed to be the complex of three steps of the analcime type, each step beginning at the room temperature, at 150°C. and at 300°C..

Scolecite: Most part of water of crystallization of scolecite is lost as natrolite type at 200°C. and 370°C..

Apophyllite: The dehydration process of apophyllite resembles to that of scolecite.

(4) *The type which does not belong to any of the types above mentioned.* Epistilbite, stilbite and thomsonite belong to this type.

They show particular phenomena of dehydration. As for epistilbite more detailed investigation is necessary.

These results will be discussed in more detail in near future with related results of X-ray studies on zeolites carried out by the author and his co-worker.

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# ON CONICHALCITE FROM KITABIRA, YAMAGUCHI PREFECTURE, JAPAN*

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## *Introduction*

Four hydrated or basic arsenate minerals have been reported from Kitabira mine, Oota-machi, Yamaguchi Prefecture**, namely scorodite ($FeAsO_4 \cdot 2H_2O$)[4], olivenite ($Cu_2AsO_4(OH)$)[2][3][5][7][10], cuproadamite ($(Cu, Zn)_2AsO_4(OH)$)[6], and clinoclasite ($Cu_3(AsO_4)_2(OH)_2$)[6][7][9]. They are all fine crystals lining the druses in limonite. In addition to these we have found recently grass-green botryoidal conichalcite, a rare mineral of basic arsenate of copper and calcium, from the same locality.

## *Occurrence*

The Kitabira mine is situated at about 15 kilometers northwest of Yamaguchi City,*** Yamaguchi Prefecture. The Kitabira ore deposit of the mine is a contact-metasomatic one formed in paleozoic limestone intruded by granitic rocks. The ore consists primarily of sulphide minerals such as arsenopyrite, pyrite, pyrrhotite, chalcopyrite etc., which, at the upper zone of the deposit, altered into limonite and other oxidized products of sulphide minerals.

Conichalcite is found as thin film that covers the wall of druse

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* Studies on the arsenate minerals from Japan, Rept. 5. This investigation was carried out at the Institute of Earth Science, College of General Education, University of Tokyo and the Institute of Mineralogy, University of Tokyo. A preliminary report of this work was read at the meeting of the Mineralogical Society of Japan in Oct. 1952.

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in limonite. Sometimes, it is closely associated with the fine crystals of olivenite.

### *General characters and physical properties*

Conichalcite from the Kitabira mine has a grass-green color and has a botryoidal or reniform appearance. However, it is actually composed of minute fibrous crystals arranged in radial aggregates. The individual crystals are about 0.05 mm. long and the crust formed of them attains about 2 mm. thick. Crystal form is not observed.

Hardness, 4.5. Brittle. Streak, pale green. Subtranslucent. The specific gravity is measured as $4.323 \pm 0.005$ at 10°C. by means of a picnometer. The result is in good agreement with that obtained by Larsen and Berman[1].

### *Optical properties*

The indices of refraction were measured by the dispersion method. Because of the fibrous nature of conichalcite, the refractive index $\beta$ and the optical angle could not be determined. The resuls are given in Table 1, compared with those of conichalcite found from Bisbee and from Bristol. Under the microscope, it shows straight extinction with positive sign of elongation.

Table 1. Optical properties of conichalcite.

| | | Bisbee* | Bristol* | Kitabira |
|---|---|---|---|---|
| Refractive indices | $\alpha$ | 1.800 | 1.730 | 1.793 |
| | $\beta$ | 1.831 | —— | —— |
| | $\gamma$ | 1.846 | 1.771 | 1.834 |
| Double refraction | $\gamma-\alpha$ | 0.046 | 0.023 | 0.041 |
| Elongation | | —— | + | + |
| Pleochroism | X | Green | Nearly colorless | Green |
| | Y | Yellow-green | Pale greenish | Green |
| | Z | Blue-green | Pale bluish | Bluish green |

* After the Dana's System of Mineralogy, vol. II, 7th Ed..

### *Chemical composition*

The specimen was first tested chemical-microscopically, potassium iodide solid being used for the determination of arsenic, and ammonium mercuric thiocyanide solution for copper. Then, crushed specimens were handsorted under the biocular microscope. An examination under the high-power microscope revealed that it contained no appreciable amount of impurity.

The procedure of analysis follows:

A sample, 0.033840 g. was used for the determinations of the $H_2O(-)$, insoluble residue, $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $As_2O_5$, CuO, ZnO, MgO and CaO. The $H_2O(+)$ was determined by the Penfield method.

The results are given in Table 2 compared with the theoretical composition of conichalcite. The atomic ratio calculated from the weight percentage is shown in the same table. The chemical composition is represented by the formula $(Mg, Ca, Cu)_{2.0}(AsO_4)_{1.0}(OH)+1/6\,H_2O$, where the ratio of Mg : Ca : Cu is 3 : 11 : 14. Accord-

Table 2. Chemical analysis and atomic composition of conichalcite.

| | $CaCu(AsO_4)(OH)$ | Kitabira | | | | |
|---|---|---|---|---|---|---|
| | Wt.% | Wt.% | Mol. prop. | Atom. rat. | | |
| $As_2O_5$ | 44.27% | 44.30% | .193 | As | 1.00 | |
| CuO | 30.65 | 30.22 | .380 | Cu | 0.98 | |
| ZnO | | 0.11 | .001 | Zn | —— | 2.01 |
| CaO | 21.61 | 17.07 | .304 | Ca | 0.79 | 2.01 |
| MgO | | 3.67 | .091 | Mg | 0.24 | |
| $Fe_2O_3$ | | 0.07 | .0004 | OH | 1.00 | |
| $Al_2O_3$ | | 0.20 | .002 | $H_2O$ | 0.17≒1/6 | |
| $SiO_2$ | | tr. | —— | | | |
| $SO_3$ | | 0.04 | —— | | | |
| Insol. | | 0.08 | —— | | | |
| $H_2O(+)$ | 3.47 | 4.46 | .248 | | | |
| $H_2O(-)$ | | 0.18 | .010 | | | |
| Total | 100.00 | 100.40 | | | | |

(Analysed by H. Minato, 1952)

ingly, the mineral may be specified as a magnesium-rich conichalcite. It is to be noted that the analysis shows a small amount of water in excess of the calculated value, an excess usually observed in

Table 3. X-ray powder pattern of conichalcite.

| | Tintic | | | Kitabira | | | Theoretical value | |
|---|---|---|---|---|---|---|---|---|
| | I | θ (CuKα) | d (meas.) | I | θ (CuKα) | d (meas.) | (hkl) | d (calc.) |
| 1 | 2 | 12.9° | 3.11kX | 2 | 12.4° | 3.09kX | 2* | |
| 2 | 8 | 14.27 | 3.12 | 8 | 14.19 | 3.12 | (026) | 3.14kX |
| 3 | 10 | 15.66 | 2.855 | 9 | 15.66 | 2.855 | (220) | 2.88 |
| 4 | 9 | 17.32 | 2.590 | 8 | 17.37 | 2.582 | (202) | 2.595 |
| 5 | 8 | 18.72 | 2.400 | 6 | 18.80 | 2.390 | (230)<br>(310) | 2.420<br>2.387 |
| 6 | 2 | 19.38 | 2.302 | 1 | 19.70 | 2.284 | (040) | 2.300 |
| 7 | 3 | 22.23 | 2.037 | 5 | 22.00 | 2.058 | (222) | 2.055 |
| 8 | 1 | 23.20 | 1.763 | 1 | 23.50 | 1.739 | 11* | |
| 9 | 6 | 24.95 | 1.824 | 5 | 24.85 | 1.836 | (331) | 1.842 |
| 10 | 5 | 25.49 | 1.794 | – | — | — | (042)<br>(023)<br>(150) | 1.803<br>1.800<br>1.797 |
| 11 | 7 | 26.71 | 1.714 | 7 | 26.54 | 1.724 | (151)<br>(203) | 1.711<br>1.727 |
| 12 | 7 | 28.63 | 1.606 | 7 | 28.51 | 1.614 | (430)<br>(133) | 1.611<br>1.607 |
| 13 | 2 | 29.53 | 1.563 | – | — | — | (402)<br>(052) | 1.569<br>1.562 |
| 14 | 6 | 30.35 | 1.524 | 3 | 30.14 | 1.533 | (060)<br>(303) | 1.533<br>1.532 |
| 15 | 3 | 31.82 | 1.461 | – | — | — | (510)<br>(004) | 1.465<br>1.460 |
| 16 | 3 | 32.82 | 1.432 | 1 | 32.39 | 1.439 | | |
| 17 | 6 | 34.03 | 1.377 | 3 | 34.07 | 1.375 | | |
| 18 | 6 | 36.77 | 1.287 | 2 | 36.52 | 1.294 | | |
| 19 | 6 | 39.71 | 1.204 | 4 | 39.39 | 1.212 | | |
| 20 | 3 | 42.21 | 1.146 | – | — | — | | |
| 21 | 3 | 44.29 | 1.102 | 1 | 44.38 | 1.100 | | |
| 22 | 2 | 47.77 | 1.039 | – | — | — | | |
| 23 | 2 | 50.27 | 1.001 | – | — | — | | |

* Diffraction lines of CuKβ.

botryoidal mineral. The existence of $Fe_2O_3$ and $Al_2O_3$ is considered to be due to the not-ascertained impurities that the specimens may possibly contain.

### *X-ray examinations*

The powder photograph (camera radius 35 mm., unfiltrated Cu K$\alpha$ radiations) of conichalcite from Kitabira was compared with that of the specimen from Tintic, Jubao Co., Utah, and a close agreement is found between them. Observed intensities and measured spacings are listed in Table 3 compared with the theoretical values that were calculated on the basis of the values $a_0$=7.42 kX, $b_0$=9.20 kX, $c_0$=5.85 kX[1)8)]. The rotation method (Cu K$\alpha$ 1.54Å.) was also applied, measuring the $c_0$ length to be 5.5–6.0 kX, the other lengths having been not determined, on account of the fibrous nature of the crystals examined.

### *Summary*

Conichalcite from the Kitabira mine, the first occurrence of the mineral in Japan, has been investigated by the chemical, optical and X-ray methods. It is a magnesium-rich conichalcite, with Mg replacing Ca in part.

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# SUANITE, A NEW MAGNESIUM BORATE MINERAL FROM HOL KOL, SUAN, NORTH KOREA

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ABSTRACT

A new mineral from the Hol Kol mine, North Korea of the composition $Mg_2B_2O_5$, named suanite, has been described. The mineral is found usually as fibrous aggregates associated with kotoite and other borate minerals in marble which borders the gold- and copper-bearing diopside-clinohumite skarn mass. The crystal usually elongated parallel to [010] is monoclinic with the following dimensions: a=12.10Å., b=3.12Å., c=9.36Å., β=104°20′ (Weissenberg photographs, CuKα λ=1.54Å.). The space group $C_{2h}^5$-$P2_1/a$. The unit cell contains 4[$Mg_2B_2O_5$]. Colourless. Hardness 5½. Sp. gr. 2.91. Opt. properties: α=1.596, β=1.639, γ=1.670 γ-α=0.074, 2V=70° (negative); r>v, weak; X//b. The chemical analysis by N. Saito and N. Kokubu follows, $SiO_2$ 0.60, $Al_2O_3+Fe_2O_3$ 0.95, MgO 46.63, CaO 5.06, $B_2O_3$ 40.08, $CO_2$ 5.01, $H_2O(+)$ 0.90, $H_2O(-)$ 0.23, total 99.46%. After deduction of $CaCO_3$ and other impurities, MgO 53.7, $B_2O_3$ 46.3% against the theoretical composition MgO 53.66, $B_2O_3$ 46.34%. The mineral is not easily affected by cold HCl. The X-ray powder diagram of the mineral is very similar to but definitely different from, that of the artificial $Mg_2B_2O_5$, to which it is converted when heated up to 1,000°C.

## *Introduction*

In 1939 during the course of a study of the gold- and copper-bearing skarn minerals from the Hol Kol mine the writer found among other borate minerals a mineral, possibly a borate too, which could not be identified with any known one. However, the material available for investigation was so scarce that only its optical properties could be determined with certainty under the microscope. By 1943 after a revisit by the writer of the district material enough for further study had been accumulated and a chemical analysis

was executed. It turned out to be a magnesium pyroborate roughly of the composition $2MgO \cdot B_2O_3$. A brief account was then given, tentatively giving it a new mineral name, suanite.[13]

An X-ray study by Takeuchi[7] which was made and published prior to the completion of our study has revealed that the crystal structure of the mineral is composed of the pyroborate molecular groups, $B_2O_5$.

The writer gives below a detailed mineralogical description of the mineral.

### *Occurrence and paragenesis*

The Hol Kol* gold copper mine is located in the Suan gold mining district[12], Suan County, Hwanghae-do,** about 75 kilometers east-south-east of the city of Pyongyang,*** the capital of North Korea. We found in the marble that predominates in the district such boron-bearing minerals as ludwigite and warwickite as well as kotoite, a new mineral also first described by the writer[4][10][11]. Acicular or prismatic crystals of suanite in radiated masses and in subparallel intergrowths are embedded in the kotoite-marble and are usually associated with beside borate minerals clinohumite, spinel and calcite. The intimate association of suanite with other magnesium-bearing borates having similar crystal structures[2][5][6][8] is remarkable. The occurrence of warwickite will be described in a separate paper. A secondary borate mineral, probably szaibelyite, is also found along cracks of suanite.

### *Physical and optical properties*

Suanite is white in colour and translucent and perfectly colourless in thin section. Its luster is silky to pearly. Its hardness is 5.5 and its specific gravity measured is 2.91 (suspension method). Difficult to fuse.

Suanite is optically biaxial and negative. Its fibers are parallel

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to b and X. Indices of refraction were determined by immersion method;

$\alpha$=1.596, $\beta$=1.639, $\gamma$=1.670, $\gamma-\alpha$=0.074 and $2V_a$=70°. Dispersion is r > v, weak. (Table 1)

Crystallographic characters of suanite cannot easily be determined as its fibers are usually too slender. Under the microscope the slender crystals nearly cut parallel to (010), that is to say, being nearly perpendicular to b-axis show monoclinic crystal outlines as shown in Fig. 1 (Plate I). Facial angles were measured under the microscope after rendering by means of a universal stage the parallel [010] edges, along which the crystals are usually elongated, vertical. The outlines of the crystal and their relation to the optical orientations are shown in Fig. 3.

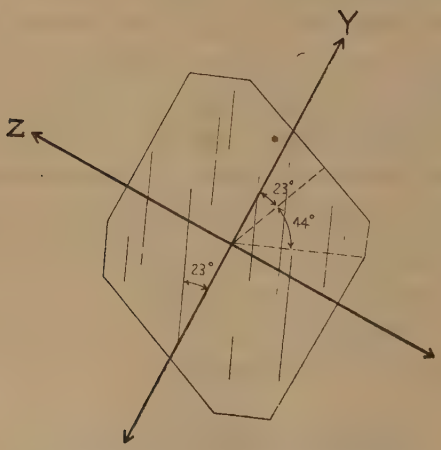


Fig. 3. The outlines of a crystal of suanite cut perpendicular to b-axis and their relation to the optical orientations.

The slender crystals of suanite separated from the fibrous aggregates were studied with rotation and Weissenberg photographs by Y. Takeuchi and its crystal structure has already been determined

by him[7] in 1952. The result of his structural studies is as follows: the unit cell has the dimensions $a_0=12.10\pm0.05$Å., $b_0=3.12\pm0.02$Å., $c_0=9.36\pm0.05$Å., $a_0:b_0:c_0=3.880:1:3.000$, $\beta=104°\,20'\pm30'$, and contains four molecules of $Mg_2B_2O_5$. Its space group is $C_{2h}^5$-$P2_1/a$. Calculated specific gravity is 2.89 against 2.91 measured.

Table 1. Comparison of some properties of kotoite, suanite, artificial pyroborate, and szaibelyite.

| | Kotoite | Suanite | Artificial Pyroborate | Szaibelyite |
|---|---|---|---|---|
| Locality | Hol Kol | Hol Kol | Synthesized by Davis and Watanabe | (After Schaller) |
| Colour | colourless | colourless | colourless | colourless |
| $\alpha$ | 1.652 | 1.596 | 1.589 | 1.575 |
| $\beta$ | 1.653 | 1.639 | 1.660 | 1.646 |
| $\gamma$ | 1.673 | 1.670 | 1.674 | 1.650 |
| $\gamma-\alpha$ | 0.021 | 0.074 | 0.085 | 0.075 |
| 2V | 21° | 70° | 40° | 25° |
| Opt. sign | (+) | (−) | (−) | (−) |
| Opt. orient. | $Z/\!/C$, $op/\!/(010)$ | $X/\!/b$ | $X\perp$cleavage | |
| Cleavage | (110) | $/\!/b$ | 2 directions | |
| Hardness | $6\frac{1}{2}$ | $5\frac{1}{2}$ | | |
| Sp. G. (meas.) | 3.11 | 2.91 | | 2.65 |
| Sp. G. (Calc.) | | 2.89 | | |
| $a_0$ | 5.38 Å | 12.10 Å | 3.12 Å | |
| $b_0$ | 8.40 Å | 3.12 Å | 5.93 Å | |
| $c_0$ | 4.48 Å | 9.36 Å | 9.03 Å | |
| Axial angles | | $\beta=104°20'$ | $\alpha=103.9°$<br>$\beta=90.9°$<br>$\gamma=92.0°$ | |
| Space group | $D_{2h}^{12}$-Pnmn | $C_{2h}^5$-$P2_1/a$ | n. d. | n. d |
| Chem. Comp. | $3MgO\cdot B_2O_3$ | $2MgO\cdot B_2O_3$ | $2MgO\cdot B_2O_3$ | $2MgO\cdot B_2O_3\cdot H_2O$ |

### *Chemical composition*

It was very difficult to isolate pure materials for analysis due to the close association of suanite with clinohumite, szaibelyite and calcite. When the finely powdered suanite is treated by hydrochloric acid it is gelatinized, although the mineral is somewhat difficultly soluble in the cold and dilute acid.

Carefully separated fibrous mass of the mineral was first analyzed by K. Isono in the laboratory of the Geological Survey of Japan, by the courtesy of Dr. S. Yamane, then Director of the Survey. Treatment of the sample with HCl showed effervescence of $CO_2$. The result of the analysis is given in Table 2, No. 1.

Table 2. Chemical analyses of suanite

| | 1 | 2 | 2a | 2b | 3 | 4 | 5 |
|---|---|---|---|---|---|---|---|
| | % | % | | | % | % | % |
| $SiO_2$ | 0.70 | 0.60 | 0.0100 | | 0.80 | | |
| $Al_2O_3$ | 0.97 | 0.95 | 0.0095 | | 0.63 | | |
| $Fe_2O_3$ | 0.33 | | | | | | |
| MgO | 46.48 | 46.63 | 1.1565 | 1.1270 | 50.64 | 53.66 | 47.91 |
| CaO | 3.70 | 5.06 | 0.0902 | | 1.52 | | |
| $Na_2O$ | 0.90 | — | — | | | | |
| $K_2O$ | 0.00 | — | — | | | | |
| $B_2O_3$ | 38.20 | 40.08 | 0.5756 | 0.5756 | 42.28 | 46.34 | 41.38 |
| $CO_2$ | 5.70 | 5.01 | 0.1139 | | | | |
| $H_2O(+)$ | 3.50 | 0.90 | 0.0500 | | 3.87 | | 10.71 |
| $H_2O(-)$ | | 0.23 | 0.0128 | | 0.19 | | |
| Total | 100.48 | 99.46 | | | 99.93 | 100.00 | 100.00 |

1. Suanite containing a small amount of calcite. Analyst K. Isono, Geol. Surv. of Japan (1942).
2. Suanite containing a small amount of calcite. Analysts N. Saito and N. Kokubu (1948).

2a. Molecular ratios.

2b. Less $Mg_2SiO_4$, Mg (Al, Fe)$_2O_4$ and $CaCO_3$.

3. Suanite containing szaibelyite. Analysts N. Saito and Kokubu (1949).
4. Calculated composition of suanite, $2MgO \cdot B_2O_3$.
5. Calculated composition of szaibelyite, $2MgO \cdot B_2O_3 \cdot H_2O$.

In order to know the nature of water found in the analysis No. 1, the materials separated from other samples were analyzed by N. Saito and N. Kokubu at the Kyushu University in 1949. A small amount of calcite was still contained in the analyzed materials. The analytical results were also given in Table 2, Nos. 2 and 3.

After reducing $CaCO_3$, $Mg_2SiO_4$ and $Mg(Al, Fe)_2O_4$ as impurities, the analysis in column 2 gives molecular ratio $[MgO]:[B_2O_3]=1.96:1.00$, which agrees well with the formula $2MgO \cdot B_2O_3$ or $Mg_2B_2O_5$.

Higher values for $H_2O$ in column 1 and 3 attributable to the presence of secondary szaibelyite in suanite aggregates.

### *Thermal study of suanite*

The differential thermal analysis has been carried out on pulverized specimens of suanite (Fig. 4C). The curve shows an endothermic peak at 630°C.. X-ray powder patterns obtained from the suanite heated to 1000°C. and artificial $Mg_2B_2O_5$ by means of Phillips X-ray spectrometer show that both materials are identical in structure. It may therefore be assumed that at 630°C. the natural monoclinic suanite is transformed into triclinic $Mg_2B_2O_5$. On the other hand, Takeuchi, from his X-ray study has concluded that magnesium pyroborate $Mg_2B_2O_5$ is dimorphous.

As an appreciable amount of water had been always reported as the results of chemical analysis of suanite the nature of the water was studied by heating its pulverized sample on a thermobalance at Tokyo Institute of Technology up to 900°C. (Fig. 4A). The thermal curves show that only a loss in weight takes place gradually up to 700°C.. However, this increases rather abruptly between 700°~900°C.. This is probably due to the presence of small amounts of szaibelyite ($2MgO \cdot B_2O_3 \cdot H_2O$) and calcite in the sample. It is to note that the dehydration temperature of szaibelyite is about 670°C. and the dissociation temperature of calcite is 880°C..

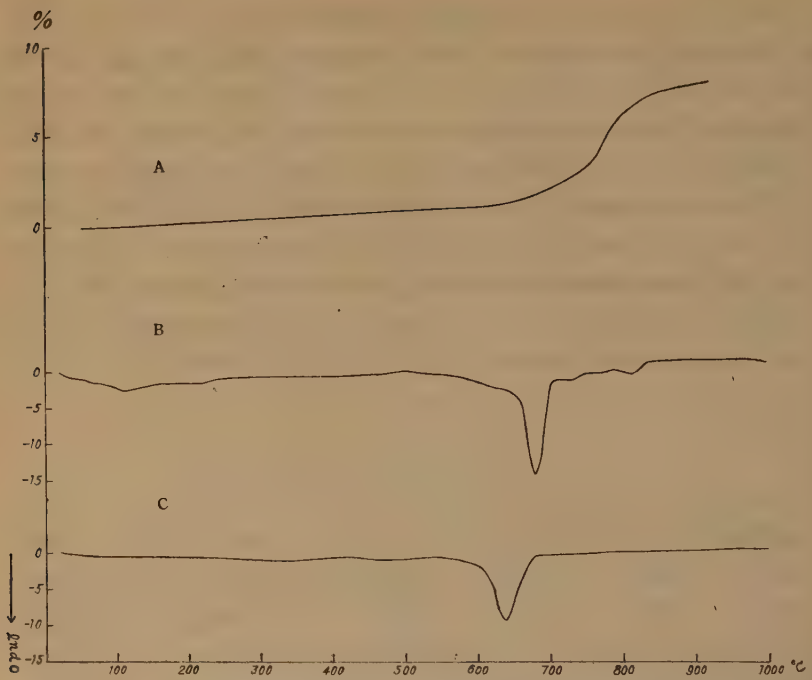


Fig. 4. A) Dehydration curve of the sample consisting mainly of suanite with small amounts of calcite and szaibelyite.
B) Differential thermal analysis curve of szaibelyite from Rézbánya. An endothermic peak at 670°C. is very marked.
C) Differential thermal analysis curve of nearly pure suanite which shows a small endothermic peak at 630°C. probably due to the inversion of natural monoclinic suanite to triclinic magnesium pyroborate.

## *Synthesis*

The first synthesis of $Mg_2B_2O_5$ has been reported by W. Guertler[3] in 1904. Later N. A. Toporov and P. F. Konovalov[9] and also H. M. Davis and M. A. Knight,[1] who studied the binary system $MgO$–$B_2O_3$, could obtain three binary compounds of magnesium-oxide and boric acid: $MgO \cdot B_2O_3$ (metaborate), $2MgO \cdot B_2O_3$ (pyroborate) and $3MgO \cdot B_2O_3$ (kotoite, orthoborate). Synthesized crystals of the magnesium pyroborate was studied optically by Davis and Knight.

The magnesium pyroborate was synthesized also by the writer by cooling slowly fused mass of MgO and $B_2O_3$ in the proportion 1:1. The product was studied with X-ray by Y. Takeuchi. His result shows that the artificial $Mg_2B_2O_5$ is triclinic having nearly the same structure with $Co_2B_2O_5$. Although no artificial monoclinic $Mg_2B_2O_5$ has yet been reported till now, as stated before, the natural suanite crystals when heated to 1000°C. are reduced into fine aggregates that show the same powder-pattern as the artificial pyroborate.

*Acknowledgements*

The writer wishes to express his sincere thanks to Professor T. Ito of the University of Tokyo and Professor H. M. Davis for their helpful suggestions and aids during the course of the present investigation and to Prof. Dr. Keith of the Pennsylvania State College, Dr. Y. Takeuchi and Mr. S. Takasu of the University of Tokyo for their assistances in X-ray studies. Further acknowledgements also are made to Dr. S. Yamane, Dr. N. Saito and Mr. N. Kokubu for their kindness in chemical analyses of minerals, and to Prof. T. Sudo and Mr. M. Kimura of the University of Tokyo, Mr. H. Yamada and Mr. S. Iwai of the Tokyo Institute of Technology for their kindness in thermal studies on suanite.

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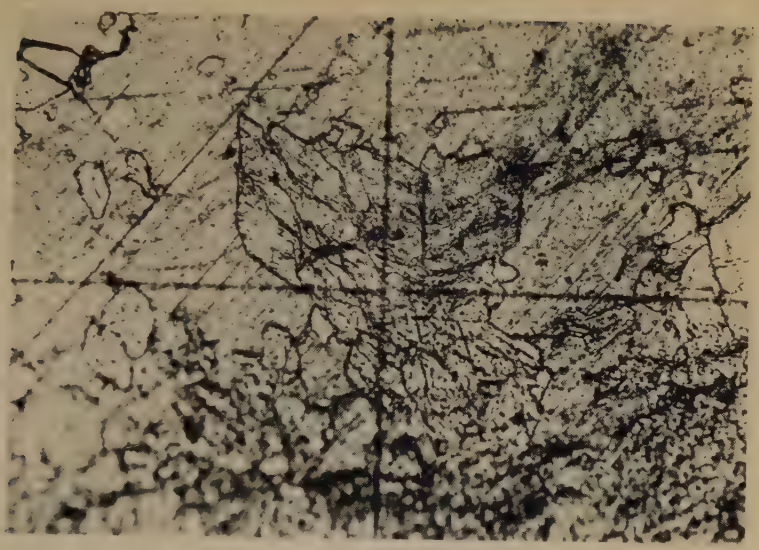

Fig. 1. Suanite $\perp$b ×63.

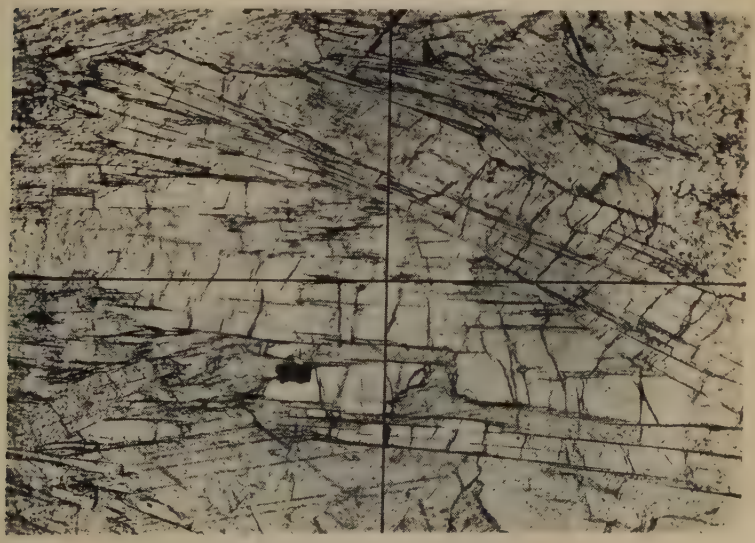

Fig. 2. Suanite $/\!/$b ×50.

MINERALOGICAL JOURNAL, VOL. 1, NO. 1, PP. 63-65, SEPTEMBER, 1953

## SHORT COMMUNICATIONS

# RECUEIL MINÉRALOGIQUE (I)

JUN ITO

*l'Institut de Minéralogie, Université de Tokyo.*

### (1) *Épidote de Munam*

L'épidote de Munam* prés de Sūan**, Corée du Nord a été découverte par Takéo Watanabé, professeur de l'Institut de Géologie, dans la zone du contact métamorphique entre calcaire et granit. Les minéraux associés sont grenat, quartz et calcit. Les cristaux mesurent 4×10×4 mm.. Les formes observées par le goniomètre aux deux cercles sont: *a* (100), *c* (001), *r* ($10\bar{1}$), *i* ($10\bar{2}$), *e* (101), *n* ($11\bar{1}$), *o* (011), *u* (210), *b* (010) et *y* ($21\bar{1}$) (Table 1). Les faces de *r* sont les plus distinctement dévelopées (Fig. 1). Voici les constantes optique déterminées: Biaxe négatif avec 2V=72°, $n_p$=1.739, $n_m$=1.770, $n_g$=1.787 (Na). L'orientation est $n_m$ sur (010) avec $n_g \wedge c$=4°.

Table 1. Les angles mesurés au goniomètre aux deux cercles.

| | ρ (observé) | φ (observé) | ρ (calculé) | φ (calculé) |
|---|---|---|---|---|
| *a* (100) | 90° 0′ | 90° 0′ | 90° 0′ | 90° 0′ |
| *c* (001) | 89 56 | 154 56 | „ | 154 37 |
| *b* (010) | 0 14 | —— | 0 0 | —— |
| *r* ($10\bar{1}$) | 90 24 | 39 10 | 90 0 | 38 18 |
| *i* ($10\bar{2}$) | 90 36 | 9 51 | „ | 8 57 |
| *e* (101) | 90 23 | 118 40 | „ | 119 54 |
| *n* ($11\bar{1}$) | 35 38 | 37 25 | 35 5 | 38 18 |
| *o* (011) | 32 54 | 155 10 | 31 43 | 154 37 |
| *u* (210) | 54 52 | 89 20 | 54 28 | 90 0 |
| *y* ($21\bar{1}$) | 52 40 | 64 51 | 51 41 | 64 2 |

* 門岩 (formerly the Moonbowie mine) ** 遂安

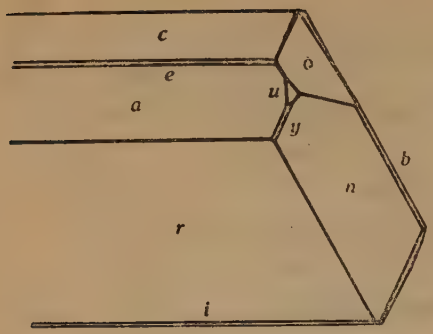


Fig. 1. Épidote de Munam.

Dispersion $\rho > \nu$. Le plan des axes optiques est (010). Pléochroisme: $n_p$ sans couleur, $n_m$ pâle-jaune et $n_g$ verdâtre-jaune.

L'analyse du minéral dont la densité est de 3.5 ($CCl_4$) a été effectuée par l'auteur: $SiO_2$ 36.75%, $TiO_2$ nil, $Al_2O_3$ 21.74%, $Fe_2O_3$ 16.18%, FeO 0.27%, MnO 0.11%, MgO nil, CaO 22.18%, $Na_2O$ nil, $K_2O$ nil, $H_2O(+)$ 1.94%, $H_2O(-)$ 0.53%, total 99.80%. La formule moléculaire calculée, $Ca_{1.9}Fe_{1.0}Al_{2.0}Si_{3.0}O_{12.0}(OH)_{1.0}$, se conforme presque rigoureusement à celle d'une épidote la plus ferrugineuse dont la proportion Fe : Al est 1 : 2.

## (2) *Épidote de Takéshi*

Les cristaux de l'épidote de Takéshi, Préfecture Nagano, Japon sont très connus. On les trouve à l'interieur des concrétions (nom populaire: "yakimochi-ishi") qui se forment dans le tuff volcanique altéré. Les cristaux, mesurant 1×5×1 mm., ont été déja décrits par Nobuo Katayama[1] (1935) qui observa les formes suivantes: *a* (100), *c* (001), *i* ($10\bar{2}$), *r* ($10\bar{1}$), *e* (101) et *u* (210) (Fig. 2). Les propriétes optiques ont été mesurées: Biaxe négatif avec 2V = 72°, $n_p$ = 1.734, $n_m$ = 1.764, $n_g$ = 1.780 (Na). L'orientation est $n_m$ sur (010) et $n_g$ sur (100). Dispersion: $\rho > \nu$. Le plan des axes optiques est

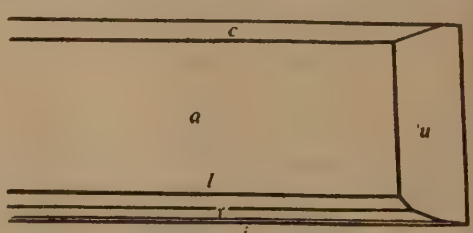


Fig. 2. Épidote de Takéshi (apres Katayama).

1) Ito, T.: Beiträge z. Min. v. Japan, N. F. 1, 207 (1935).

(010). Pléochroisme: $n_p$ brunaitre-jaune, $n_m$ verdâtre-jaune et $n_g$ vert.

La composition chimique du minéral dont la densité est de 3.4 ($CCl_4$) est la suivante (analysé par l'auteur): $SiO_2$ 36.89%, $TiO_2$ nil, $Al_2O_3$ 20.94%, $Fe_2O_3$ 15.92%, FeO 0.20%, MnO 0.13%, MgO 0.14%, CaO 23.00%, $Na_2O$ et $K_2O$ p.d., $H_2O$ (+) 1.93%, $H_2O$ (−) 0.13%, total 99.28%. La formule moléculaire obtenue, $Ca_{2.0}Fe_{1.0}Al_{2.0}Si_{3.0}O_{12.0}(OH)_{1.0}$, montre que le minéral est aussi une épidote la plus ferrugineuse comme celle de Munam cidessus.

*Manuscript received May 14, 1953*

MINERALOGICAL JOURNAL, VOL. 1, NO. 1, PP. 66-68, SEPTEMBER, 1953

# PARTICLE SHAPE OF A CERTAIN CLAY OF HYDRATED HALLOYSITE, AS REVEALED BY THE ELECTRON MICROSCOPE

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As the writer previously reported[1)2)3)] mineralogical properties of hydrated halloysite (endellite), which is found in association with sulfur and/or pyrophyllite deposits, agree well with the typical data reported in the literatures, for example, its electron micrograph shows that it consists of hollow tubes; however, hydrated halloysite altered from pumice tuff shows slightly different properties from the typical type; for example, its electron micrograph reveals that it consists of grains.

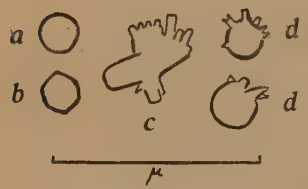


Fig. 1

Recently, the writer has ascertained fine textures of the electron micrograph of a specimen of hydrated halloysite altered from pumice tuff; the reference specimen is "Taneichi clay" from Taneichi-mura, Kokonohe-gun, Iwate Prefecture. (Fig. 1 and Pl. I).

The electron micrograph shows that the clay consists of rounded grains (0.1 microns in mean size) and fine fibers (0.03~0.1 microns in mean size). The shape of each individual is classified into the following types (Fig. 1): (a) rounded grains, (b) rounded grains with pseudo-hexagonal outlines, (c) nearly radial aggregates of fine fibers, and (d) sugar-plum-like grains, that is, extremely fine fibers jut out as radial manner from rounded grains.

The electron micrograph shows that fine fibers are found in association with rounded grains. Radial aggregates of fine fibers, in

places, seem to grade into rounded grains, namely, the rounded shape seems to be formed partly by a confused aggregate of extremely fine fibers.

Generally speaking, electron micrographs of amorphous or nearly amorphous materials, such as amorphous carbon and/or allophane, consist of rounded grains. In the light of the general concept, it is also suggested that the rounded grains now under consideration may include allophane, which may be concealed in grains mixing with extremely fine fibers. Indeed, the X-ray and thermal studies suggest the existence of allophane mixing with hydrated halloysite in certain specimens including the clay now under consideration. The summary of the results is as follows.[2)3)]

The X-ray powder pattern agrees well with that of the typical hydrated halloysite; the basal reflection shifts from 10.1 kX to 11.0 kX by the ethylene glycol treatment; but, commonly, a longer exposure time was needed to obtain measurable powder lines than in the case of the typical type.

The general feature of the D. T. A. curve agrees well with that of the typical type, that is, three thermal peaks were revealed: the first endothermic peak between 100°C. and 200°C., the second endothermic peak between 500°C. and 600°C., and the last exothermic peak between 900°C. and 1000°C.. Besides these three peaks, any other peaks are not recognized. But, the temperatures of both of the second and third peaks are lower, the amplitude of the first peak is commonly larger, and the amplitudes of the second and the last peaks are smaller than those of the typical data. The ratio of the area of the last peak to that of the second peak is commonly larger than that of the typical type. These differences were recognized among thermal curves recorded under the same rate of heating. Furthermore, in certain thermal curves, the last peak shows a double exothermic sign. It is also a noteworthy fact that the treatment by piperidine caused two exothermic peaks to be revealed separatedly from the three peaks mentioned above; one of these exotherms is at

about 300°C. and the other is between 400°C. and 500°C., both of which agree well with two exotherms yielded in the thermal curve of allophane by the pre-treatment with piperidine[4].

The X-ray and thermal behaviours mentioned above seem to be appropriately interpreted by the existence of allophane mixed with hydrated halloysite.

In conclusion, the electron micrograph now obtained will give a further confirmation of an intimate genetical relation between extremely fine hydrated halloysite and allophane, and may suggest an incipient stage of the crystallization of hydrated halloysite.

The electron micrograph were taken at the University of Tokyo and also at the Sophia University, Tokyo. The writer is indebted to Mr. H. Takahashi, Chemical Institute, Faculty of Science, University of Tokyo, and also to Professor E. Shibata, Sophia University.

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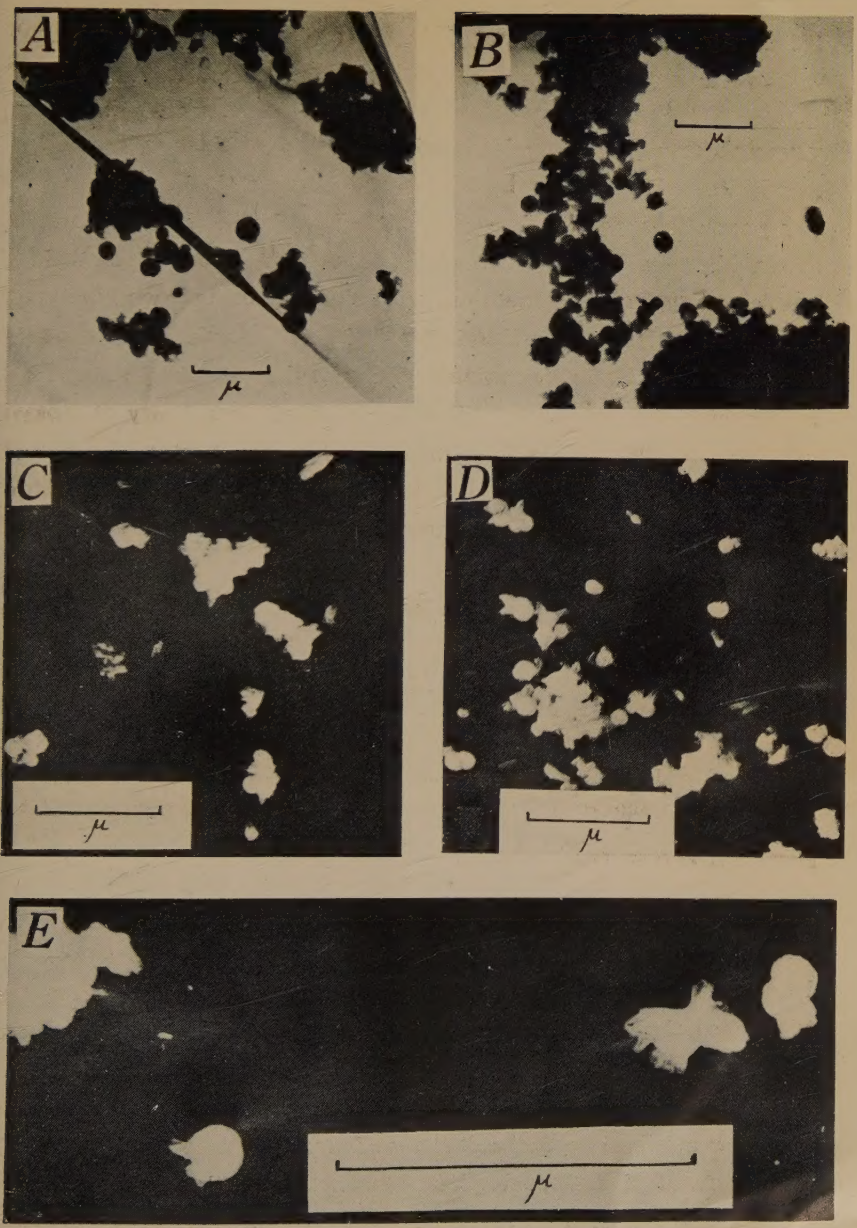
*Manuscript received June 18, 1953*




Electron micrographs of "Taneichi clay" under various magnifications.
(C), (D) and (E): Cr shadowed.

# Contents of "KOBUTSUGAKU ZASSHI,"

Journal of the Mineralogical Society of Japan

*in Japanese*

---

VOL. 1, NO. 3 (May, 1953)

*Original Articles*

A Study on White Tourmaline from the Kanakura Mine, Nagano Prefecture.....H. Takeshi...105

Gahnite from a Pegmatite in Nogisawa Village, Fukushima Prefecture .....K. Omori and S. Hasegawa...113

On the Pyromorphite from the Taikyu Mine, Hokkaido ..... .....K. Muta and T. Ishimori...117

On Adamite, Cuproadamite and Olivenite from Japan .....H. Minato...125

*Short Communications*

An Additional Crystal Face of the Topaz from Naegi, Gifu Prefecture .....J. Kitahara...142

Communications on Minerals of Japan (Part I) .....Mumeikai Group...144

1. Diopside from Kanagasaki, Saitama Prefecture
2. Actinolite from Daishoji, Saitama Prefecture
3. Ilmenite from Ishikawa, Fukushima Prefecture .....K. Sakurai and T. Ashizawa

*Reviews*

Recent Studies on Polymorphism .....B. Yoshiki...148

Professor Paul Niggli.....T. Ito.....161

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# Contents of "KOBUTSUGAKU ZASSHI,"

## Journal of the Mineralogical Society of Japan

*in Japanese*

---

### Vol. 1, No. 1 (September, 1952)


*Addresses*

On the Metamict Phenomena ..... J. Takubo... 1

On the Imperfections of Crystals ..... Z. Harada...13

The Scope of Clay Mineralogy ..... T. Sudo.....26


---

### Vol. 1, No. 2 (January, 1953)


*Original Articles*

On the Tetrahedrites from Western Hokkaido ..... M. Ishibashi...45

On Tscheffkinite from Shiroishi, Kyoto Prefecture, Japan .....

..... J. Takubo and S. Nishimura...51

On the Distribution of Radium in Pegmatite Minerals found in Naka District, Kyoto Prefecture, Japan ..... J. Takubo and M. Tachikawa...57

*Short Communications*

On the Fibrous Opal from Ishiyasuba, Suwa-iron-mine, Nagano Prefecture ..... H. Minato...67

Chemical Composition of Bismuthinite from the Miyatamata Mine, Akita Prefecture ..... H. Ohmachi and S. Matsuda...71

An Apparatus for Optical Measurement of Minerals with a Photomultiplier ..... N. Katayama and Y. Sato...73

On the So-called "Refractory Clay" and its Clay Mineral from Akabira, Hokkaido ..... M. Takayasu...78

*Reviews*

An Apparatus for Differential Thermal Analysis ..... T. Sudo...84

Synthetic Minerals ..... H. Inuzuka and T. Imai...90